

**Oxidative Dehydrogenation of Propane Using Rhénia Supported
on Al₂O₃ and TiO₂**



*A thesis submitted in Partial Fulfillment of the
Requirements for the Degree of
Master of Technology*

by

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to the

**Department of Chemical Engineering
Indian Institute of Technology Kanpur.**

April 2001

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CERTIFICATE

It is certified that the work contained in the thesis entitled **Oxidative Dehydrogenation of Propane Using Rhénia Supported on Al₂O₃ and TiO₂** by **Wadje Rajendra B.** has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.



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Acknowledgements

I remain indebted to Dr. Goutam Deo, my thesis supervisor and *guide*.

Among the ChE faculty members, I express my gratitude to Prof. D. P. Rao, Prof. P. K. Bhattacharya, and Dr. R. Ravi for the help and guidance extended by them.

I express my most special thanks to *chechy* Maymol for tons of things.

I express bright thanks to bright CL guys like Kushal, Anoop, and Vineet, who have been helpful in not-so-bright time.

A note of thanks to Deba, for helping me set up *this* computer; to my labmates Sravan and Rohit for being cooperative in sharing resources; and to guys like Pramod, Abhishek, Dhawal, and above all, Ashwin, for *this-n-that*. The help extended by my friend Amit during the preparation of this report is gratefully acknowledged.

Thanks are due to Tapan for what he is. And to my *b'pal* Srinivas.

IITK has been a most wonderful place- a lot of thanks to a lot of people.

Rajendra Wadje

30 April 2001

Kanpur.

Abstract

The efficacy of rhenium oxide supported on titania and alumina for the oxidative dehydrogenation of propane was studied at constant oxygen to propane ratio and constant flow rate. The catalysts were prepared by incipient wetness impregnation technique and their rhenium content was ascertained by atomic absorption spectroscopy. The catalysts were characterized using Raman spectroscopy, UV-Visible Spectroscopy, and Temperature Programmed Reduction (TPR) experiments. Results of the characterization studies were in line with expectations and conforming to the previous work. Presence of the same surface rhenium species on the titania and alumina supports was proposed. From the amount of rhenium oxide retained on the support after calcination and the TPR experiments, alumina support was inferred to have greater affinity for surface rhenium oxide species. Rhenium volatilizing from the support during the reaction was also greater for titania supported catalysts. Oxidative dehydrogenation studies using propane reveal the inherent high activity of the titania support for oxidation reactions. Titania supported rhenium oxide catalysts were, in general, found more active and less selective than the alumina supported rhenium oxide catalysts. This difference in activity and selectivity appears to be related to the strength/nature of the Re-O-Support bridging bond. The effect of rhenium oxide loading on the TOF was, however, difficult to establish due to volatility of the surface rhenium during reaction. Based on the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ data, where the rhenium oxide volatility was not as pronounced except for the highest loading, the TOF was relatively constant with loading.

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Supported metal oxide catalysts form a sizable section of solid catalysts. Obtained by deposition of one metal oxide on the surface of other, these show catalytic properties different from the support, the supported oxide, and the chemical compound formed between the two.

The supports used generally are high surface area stable oxides of metals and semiconductors. Commonly employed supports are Al_2O_3 , TiO_2 , SiO_2 , ZrO_2 , Nb_2O_5 , CeO_2 , etc. and mixtures of these. The supported species are oxides of transition metals like Cr, V, Ti, Mo, Co, etc.

Supported rhenium oxide catalysts are a type of supported metal oxide catalysts where rhenium oxide is present as a two-dimensional phase on the surface of oxide supports. These catalysts find a number of applications in the petrochemical and environmental industries. For example, $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ is a highly effective catalyst for olefin metathesis, a reaction of great commercial importance [1], and for the hydrosulfurization reaction [2]. $\text{Re}_2\text{O}_7/\text{TiO}_2$ catalysts is an effective catalyst for selective catalytic reduction of NO_x by ammonia [3].

1.1 Preparation of Supported Rhenium Oxide Catalysts

These catalysts are generally prepared by the incipient wetness impregnation technique [4]. The ability of this technique to give a uniform loading has been questioned [5], and alternatives have been suggested [6]. However, this method is suitable for preparation of supported rhenium oxide catalysts owing to its simplicity. This method consists of pretreatment of the support, impregnation of the support with an active species precursor, gradual drying, and calcination. The precursor used for preparation is generally a salt, NH_4ReO_4 , or an aqueous solution of perrhenic acid, HReO_4 . Among the various steps involved in preparation, the most important is the calcination step.

Calcination temperature is important since the active species is formed, dispersed, and anchored to the support during calcination. Moderate calcination temperatures are

required to decompose the precursor. Low calcination temperatures do not make the reaction of surface hydroxyls to form surface metal oxide possible. At high calcination temperatures, apart from reduction in surface area of the support, active species may react with the support if the chemical affinity is high or it may form a solid solution with the support if the miscibility is high. In addition to the support used, calcination temperatures also depend on loading and the method of loading. Actual loadings of supported Re_2O_7 catalysts are invariably less than those attempted owing to the unstable nature of surface rhenium oxide species at the calcination temperatures. At these temperatures, two unstable $[\text{ReO}_4]_{\text{ads}}$ combine to form a gaseous Re_2O_7 molecule [7]. It must be noted that, though represented as $\text{Re}_2\text{O}_7/\text{Support}$, supported rhenium oxide catalysts do not have Re_2O_7 as an active species because Re_2O_7 sublimates at 202°C , whereas the active species is firmly bound to alumina support even at 550°C [8]. Preparation method is not important as long as it does not influence the support matrix [9].

1.2 Characterization

Structure of the active species and its interaction with the support are paramount for correlating catalytic properties with structure. Owing to its use as a metathesis catalyst, $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ has been a system well studied using a plethora of characterization techniques. It is necessary to characterize a catalyst using various techniques, as different techniques, because of their distinct principle of operation, throw light on different aspects on the nature of the active site.

1.2.1 Raman Spectroscopy

Raman spectroscopy relies on changes in polarizability accompanying molecular vibrations. It is the most valuable tool for physical characterization of supported metal oxide catalysts [10,11]. This is due to low Raman activity shown by most oxide supports and the ability of this technique to distinguish between various metal oxide species that may coexist on the support. The region of interest here is $100\text{--}1100\text{ cm}^{-1}$, as most of the metal-oxygen vibrations are confined to this region. Ref. 10 is a good compilation of characterization studies using this technique. *In situ* Raman spectroscopy, which enables

study of the catalyst under actual reaction conditions has also attained considerable popularity [12].

1.2.2 IR Spectroscopy

Infrared spectroscopy relies on changing dipole moments with molecular vibrations. The present work does not employ IR studies for probing catalyst structure. However, IR studies are worth making a reference to owing to the unique information that can be obtained about surface hydroxyls and the acidic and basic character of the surfaces. The region of interest for probing surface hydroxyls using IR spectroscopy is $3200\text{--}3800\text{ cm}^{-1}$. The acidic nature of surface is diagnosed by monitoring desorption of a previously chemisorbed base probe, like ammonia, n-butylamine, or pyridine, whereas the basic properties are probed by monitoring desorption of an acid probe, like CO_2 , nitric oxide, or phenol vapor [13]. Busca has discussed the surface acidity of solid oxides and its characterization by IR spectroscopic methods in detail [14]. As far as detection of surface metal oxide phases is concerned, IR is useful, but hampered by strong absorbance by commonly used oxide supports at low wavenumbers.

1.2.3 XPS

A low analysis depth of 1-5nm gives XPS an edge over other techniques when it comes to directly probing the very first few surface layers of the solid. XPS can yield information about oxidation state and elemental composition.

1.2.4 UV-visible Spectroscopy

UV-visible operating in the diffuse reflectance mode can give information about the oxidation state and structure of surface metal oxide. However, UV-visible spectroscopy has gained limited popularity for analysis of supported metal oxide catalysts owing partly to its inability to yield conclusive data and mainly to the availability of powerful alternatives like Raman spectroscopy, IR, and XPS. The present work makes an attempt at characterizing $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ and $\text{Re}_2\text{O}_7/\text{TiO}_2$ catalysts using this technique.

Detailed introduction to the various spectroscopic techniques employed for characterization of heterogeneous catalysts is available elsewhere [11,15]

1.2.4 Temperature Programmed Reduction

Temperature programmed reduction, TPR, is a thermal analysis technique wherein an oxidic catalyst precursor is subjected to a programmed temperature rise in the presence of a reducing environment. Reaction between the sample and the reducing gas is monitored, for example, by a thermal conductivity detector (TCD). The resulting peak in the reaction rate signal is a unique, characteristic "fingerprint" of the sample and its maximum represents the temperature of maximum reaction rate. Present studies include TPR analysis of one catalyst each from the Al₂O₃ and TiO₂ supported catalysts. These catalysts are representative of the respective supported catalysts, as is expatiated later.

1.3 Oxidative Dehydrogenation

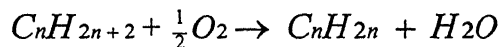
Dehydrogenation of light alkanes is a reaction of great commercial importance, as dehydrogenation of propane yields propylene, the polypropylene monomer. MTBE is an important ingredient of reformulated gasoline, production of which requires butylene, the dehydrogenation product of butane.

The dehydrogenation reaction of alkanes can be represented as:



This reaction can be carried out thermally. However, the production of alkenes is favored only at 600°C when propane and butane are the reactants. At such high temperature, side reactions such as cracking reduce the selectivity for desired compounds in addition to rapid coking of the catalyst. Moreover, this reaction is endothermic because of high heat of formation (exothermic) of lower hydrocarbons, which makes addition of heat necessary for its sustenance. Higher pressures are also required since there are a greater number of moles in the product than the reactants [16].

Most of the problems associated with dehydrogenation can be circumvented by the use of oxidative dehydrogenation. The introduction of a hydrogen acceptor into a dehydrogenation reaction medium shifts the thermodynamic equilibrium, making it virtually irreversible. The use of an acceptor with high affinity for hydrogen makes the reaction exothermic and limits coke deposition. With oxygen as the hydrogen acceptor, the reaction can be represented as-



The equilibrium constant of the above reaction can be expressed in terms of the individual Gibbs free energy of formations as given below.

$$-RT \ln K_p = \Delta G^\circ_{C_nH_{2n}} + \Delta G^\circ_{H_2O} - \Delta G^\circ_{C_nH_{2n+2}}$$

The Gibbs free energy of formation of H₂O has a high negative value. Therefore, K_p assumes a high positive value, shifting the equilibrium sufficiently far to the right that the reaction may be considered irreversible even at low temperatures. [17]

Mere addition of an hydrogen acceptor does not yield a solution, as ODH itself can proceed along two pathways. Either oxygen interacts directly with the hydrocarbon molecule or it binds to the hydrogen previously accepted. Direct incorporation of oxygen present in the reaction molecule may also occur, giving oxygenated products or total combustion. All of these processes are thermodynamically favorable. To achieve the required conversion of the alkanes to alkenes an appropriate catalyst is required. This catalyst should be tailored to significantly accelerate the abstraction of hydrogen from the hydrocarbon molecule, which is the first step in the sequence of an oxidation reaction; hinder both the nucleophilic insertion of oxygen into the molecule; and the electrophilic attack of oxygen molecules on the C-C bond to form CO₂ [17].

1.4 Literature Review

Considerable work has been done on characterization of Re₂O₇/Al₂O₃ catalysts owing to their use of metathesis catalysts. Literature abounds in the studies of ODH over various catalysts due to the high commercial importance of the ODH reaction. Significant effort has also gone into studying ODH of propane over supported metal oxide catalysts. However, no work has yet focused on supported rhenium oxide catalysts as ODH catalysts.

1.4.1 Studies on Supported Re₂O₇ Catalysts

Olsthoorn and Boelhouwer [18] studied the Re₂O₇/Al₂O₃ catalysts using IR spectroscopy. The catalysts in their studies were high Re₂O₇ loading samples prepared by aerogel method using Al₂O₃ with a surface area of 300m²/gm. It was concluded that a monolayer of Re₂O₇ existed on the surface of the support at a loading of 20% Re₂O₇ by weight.

Presence of monolayer was confirmed by observing a complete absence of IR bands representing surface hydroxyl groups. Surface Rhenia species was found to be stable and capable of undergoing oxidation and reduction cycles

The first laser Raman spectroscopic studies on the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst are due to Kerkhof et al [19]. In this study 6 to 18% $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalysts were used and the characterization was done under ambient conditions. Presence of tetrahedral ReO_4^- was suggested. It was proposed that the tetrahedral Re_2O_4 species was the only species present on the alumina support and were dynamically distorted by either the support or the surface hydroxyls. Rhenium oxide loading and the peak intensities were found uncorrelated.

Wang and Hall [5] characterized $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalysts by means of laser Raman, infrared and UV-Visible reflectance spectroscopy under dehydrated conditions. Catalysts with a rhenia content ranging from 0.3 to 2.9 atoms Re/gm were prepared by equilibrium adsorption method. The presence of a monomeric distorted tetrahedral rhenium oxide structure, possibly with C_{3v} or C_{2v} symmetry on the alumina surface, was proposed. Spectral studies also revealed that the catalyst surfaces could be dehydroxylated at high temperatures and the original state was obtained by readsorption of water. Temperature programmed reduction features revealed the reduction of most of the Rhenia to metallic state at 275°C , but a very small amount appeared to resist reduction upto 500°C .

Temperature programmed reduction studies were used by Arnoldy et al [20] to study the reduction behavior of rhenium oxide catalysts supported on SiO_2 , Al_2O_3 and carbon. For dried catalysts the surface was found to contain both monolayer type Re^{+7} species and NH_4ReO_4 crystallites which was the precursor used. High temperature calcination resulted in the decomposition of NH_4ReO_4 , formation of Re^{+7} surface phase and Re_2O_7 clusters, and rhenium loss due to sublimation of Re_2O_7 . Difference in the reducibility of the various catalysts were attributed to the strength of the Re^{+7} -support interaction which decreased in the order $\text{Al}_2\text{O}_3 > \text{SiO}_2 > \text{carbon}$. Further studies were undertaken for the determination of activation parameters for reduction of $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalysts [21].

Edreva-Kardjieva and Andreev [22] examined the surface rhenia species on alumina under oxidative precatalysis conditions by thermal analysis, XPS, IR and diffuse reflectance spectroscopic studies in order to propose a structure for the surface species. The presence of a monolayer of surface aluminum mesoperrhenate, AlReO_5 was suggested on the surface under oxidative conditions. This structure was found resisting heat and moisture and was not easily convertible to metallic rhenium. On heating the catalysts in inert atmosphere or vacuum, Re^{+6} and Re^{+4} valence states were found to coexist with Re^{+7} .

Hardcastle et al. [13] examined the interaction of the surface rhenia with the alumina support with varying rhenium oxide loading, calcination temperature and environment using laser Raman spectroscopy and XANES. Catalysts containing 0.1 to 20% Re_2O_7 were prepared by the incipient wetness impregnation technique. Under dehydrated conditions, the surface rhenia species was found to be present as $[\text{ReO}_4]_{\text{ads}}$ possessing C_{3v} symmetry. In situ studies revealed a shift in the Raman bands indicating an increase in the Re-O bond order. High calcination temperature resulted in a decrease in the surface coverage due to the removal of the surface rhenia species as gaseous dimeric Re_2O_7 .

Yide et al. [23] investigated the effect of pretreatment by helium and/or propylene on the nature of active sites in $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalysts. For He pretreatment, catalysts with higher Re ion density displayed higher activity, whereas for propylene pretreatment, catalysts with low Re ion density were found more active. Active sites created by the two pretreatments were proposed to be different. XPS studies further revealed the surface species after reaction to be composed of different valence states. However, the species responsible for above reactions was not specified.

Vuurman et al. [24] carried out Raman, IR, and TPR studies on Re_2O_7 supported on Al_2O_3 , SiO_2 , TiO_2 and ZrO_2 . Under ambient conditions, the surface rhenia species were hydrated, regardless of coverage or the support and conformed to a ReO_4^- ion structure. Under dehydrated conditions, two surface rhenium oxide species were present for Al_2O_3 , TiO_2 and ZrO_2 supports, whereas for the SiO_2 support only one species was found. The concentration ratio of the two surface species was a function of coverage and a C_{3v} symmetry was invariably present with three terminal $\text{Re}=\text{O}$ bonds and one $\text{Re}-\text{O}-$

support bond. TPR data revealed a decrease in the Re-O-support bond strength in the order $\text{Al}_2\text{O}_3 > \text{ZrO}_2 > \text{SiO}_2 > \text{TiO}_2$.

Turek et al. [25] studied acidic properties of $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalysts by IR spectroscopy. Analysis of the hydroxyl region of the IR spectra revealed a sequential depletion of the alumina OH groups with increasing rhenia loading. The more basic hydroxyls were initially depleted followed by the neutral and acidic hydroxyls. Spectra of CO_2 chemisorbed on $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ revealed the presence of five different types of CO_2 species at low loadings, whereas at higher coverages, only two of the most abundant types were found. The spectra for the 15.6% Re_2O_7 sample, 8 atoms/ nm^2 , which corresponds to almost monolayer coverage revealed no chemisorbed CO_2 species.

Spronk et al. [8] examined the effect of calcination temperature on the activity of a 6% $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst for the metathesis of propylene. An increase in activity was observed for catalysts calcined at higher temperatures. The optimum temperature was found to be between 827 to 927 °C. Optimum calcination temperature was found to depend inversely on loading. This improvement in the activity was attributed to the nearly random distribution of the ReO_4 groups on all types of sites of the alumina surface on calcination.

Kim and Wachs [26] investigated the molecular structure of 1% Re_2O_7 on supports such as Al_2O_3 , TiO_2 , ZrO_2 , SiO_2 and MgO under ambient and dehydrated conditions by Raman spectroscopy. Under ambient conditions, the surface rhenia species was found to resemble the ReO_4^- ion in aqueous solution independent of the oxide support. Under *in situ* conditions, a different surface rhenia structure was observed, which corresponded to an isolated four coordinated rhenium oxide species with three terminal $\text{Re}=\text{O}$ bonds and one bridging Re-O-support bond for all supports except MgO . Methanol oxidation studies by the same authors reveal high selectivity of $\text{Re}_2\text{O}_7/\text{TiO}_2$ for formaldehyde, which is an oxidative dehydrogenation product.

The strong acidic character of $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$, an active metathesis catalyst even at room temperature, has been the cynosure of the eyes of many researchers. Nahama et al [27] have characterized surface acidity of this catalyst by IR coupled with ammonia thermodesorption, whereas Ishikawa et al. [28] have probed into acidic properties of $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst using FTIR coupled with thermodesorption of adsorbed pyridine.

Xiaoding et al. have done significant work on Re_2O_7 supported on mixed oxides like $\text{Al}_2\text{O}_3\text{-B}_2\text{O}_3$ [29] and $\text{SiO}_2\text{-Al}_2\text{O}_3$ [30]. The group has further investigated into the effect of tetraalkyl tin promoters on the activities of Re_2O_7 on alumina [31] and on mixed oxide supports [32]. These alterations were found to increase the activity by one to two orders of magnitude.

Wachs et. al. [3] have reported the excellent redox characteristics of $\text{Re}_2\text{O}_7/\text{TiO}_2$ catalysts during the selective catalytic reduction (SCR) of NO_x with NH_3 . Methanol oxidation studies on this catalyst by the same group [33] have corroborated the redox potential. $\text{Re}_2\text{O}_7/\text{TiO}_2$ catalyst was reported to have redox capabilities comparable to those of $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst, which are industrially used for SCR of NO_x and the oxidation of o- xylene to phthalic anhydride.

Among recent studies, Wachs et al. [34] have reported a new finding of reaction induced spreading of various metal oxides onto the surface of supports, including Re_2O_7 on TiO_2 . The reaction used was methanol oxidation and the spreading was found governed by factors like temperature, gaseous component, metal oxide, and oxide support. These findings are commercially important especially for the synthesis of these catalysts.

Weckhusen et al. [35] performed *in situ* Raman spectroscopy combined with $^{18}\text{O}_2\text{-}^{16}\text{O}_2$ isotopic labeling on supported transition metal oxide catalysts, which included $\text{Re}_2\text{O}_7/\text{ZrO}_2$. The studies were done under dehydrated conditions and it was found that all supported transition metal oxides are present as monoxo (having only one metal-oxygen double bond) species on ZrO_2 .

Houalla et al. [36] determined the surface coverage of $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalysts by low temperature CO adsorption. The results were in agreement with those obtained by ion scattering spectroscopy.

Very recently, Mitra et al [37] performed comprehensive characterization studies on supported rhenium oxide catalysts. The effect of loading, support, and various additives was analyzed. They have pointed out that the shift in TPR maximum that is usually observed can owe its presence to mass transfer limitations instead of chemical heterogeneity of the support, as is usually conjectured.

1.4.2 Studies on ODH of Propane

Delmon et al. [38] have pointed out the role of homogeneous reactions in the oxidation of hydrocarbons, and the beneficial effect of water in the homogeneous propane ODH reaction.

Yasmeen [39] conducted the ODH of propane reaction over supported molybdenum oxide catalysts. It was observed that the most selective catalyst for the conversion of propane was 5% $\text{MoO}_3/\text{TiO}_2$ over which a propylene yield of 10.5% was obtained. The better selectivity of these catalysts was attributed to the change in pore structure owing to the higher calcination temperatures employed. The use of vanadium oxide as promoter resulted in an increase in the activity of the catalyst and a concomitant decrease in selectivity to propylene. The increase in residence time produced a small amount of oxygenated products and carbon oxides along with propylene

Bell et al. [40,41] have done considerable work on vanadia based catalysts, which are promising ODH catalysts. They have studied the structure and catalytic properties of supported vanadium oxide and have delved into the support effects. In their studies, a wide range surface vanadium density was used on Al_2O_3 , ZrO_2 , TiO_2 , SiO_2 and HfO_2 supports. Support surfaces predominantly covered with polyvanadate structures or small V_2O_5 clusters containing V-O-V or V=O linkages lead to high ODH rates and selectivities. This group has also studied structure and properties of vanadium oxide – zirconia catalysts for ODH of propane.

Anderson and Creaser [42] made kinetic investigations into the ODH of propane over V-Mg-O catalysts. Propane was found to react with surface oxygen species to form adsorbed propylene capable of subsequent desorption from the solid phase.

Blasco and Nieto [43] have summarized data on ODH of short chain alkanes (C_2 - C_4) over supported V_2O_5 catalysts. They have pointed out the influence of acid-base character of the support metal oxide on the nature of surface species as well as its dispersion. It was observed that reducibility, structure, and catalytic properties in the ODH of short chain alkanes were a strong function of loading and the oxide support.

Parmaliana et al [44] reported a highly effective catalyst for the ODH of propane. The catalyst used was 5% $\text{V}_2\text{O}_5/\text{SiO}_2$, which exhibited high yield, productivity, and stability.

Creaser et al [45] studied the effect of partial pressure of O_2 on the ODH of propane over V-Mg-O catalysts. These experiments were carried out with a constant propane partial pressure and a oxygen partial pressure varying over a wide range. Selectivities were compared at constant propane conversion achieved through controlling the catalyst weight. Propylene selectivity was found inversely related to oxygen partial pressure.

Grabowaski et al.[46] reported the ODH of propane over titania supported chromium and zinc oxides. The order of both activity and selectivity was found as $\text{CrTi} > \text{ZnCrTi} > \text{ZnTi}$. The activity and selectivity to propylene was found not to change markedly with increase with reaction temperature.

1.5 Rationale and Objectives

It is evident from the literature review that supported rhenium oxide catalysts, especially the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst have been extensively studied using physical characterization techniques. However, it remains to be properly characterized chemically. Moreover, no work has yet been done on the ODH of propane using these catalysts despite the reported activity displayed by $\text{Re}_2\text{O}_7/\text{TiO}_2$ for the methanol oxidation and the SCR of NO_x reaction. Thus, a more detailed study of supported rhenium oxide catalysts is required. Considerable characterization work has already been done on these catalysts [37]. Based on this work and additional characterization carried out in the present work, the nature of the surface rhenium oxide species can be determined as a function of oxide support (alumina and titania) and loadings. These well characterized catalysts will then be tested in the ODH of propane reaction and the effect of oxide support and rhenium oxide loading will be analysed. Extirpating serendipity from catalytic research by correlating catalytic activity with catalyst structure has been the *idée fixe* of a large group of the catalysis fraternity since a long time. The present work makes an attempt at the same by studying the oxidative dehydrogenation of propane over rhenia supported on titania and alumina.

1.6 Thesis Organization

Chapter two, the following chapter, focuses on the experimental details of catalyst synthesis and the physical and chemical characterization studies. Results of the experiments described in chapter two are presented in chapter three. Discussion on the results is reported in chapter four, and in chapter five, the conclusions obtained in the present study are stated. Recommendations for carrying out future work are also made and stated in chapter five. At the end are references, numbered as they appear in the text. In each chapter, the table and figures are given at the end.

2.1 Catalyst Preparation

Supported rhenium oxide catalysts were prepared by the incipient wetness impregnation technique. Pure Titania ($55 \text{ m}^2/\text{gm}$) from Degussa chemicals and γ -Alumina ($180 \text{ m}^2/\text{gm}$) from Harshaw chemicals were used as the supports. Support pretreatment consisted of making a paste of the specific support with water, drying at 100°C followed by calcination at appropriate temperature. Calcination temperatures were 500°C for the Alumina support and 450°C for the Titania support. The precursor used for creating the surface rhenium oxide species was a 60-70 % solution of perrhenic acid (HReO_4 , Aldrich, 99.98%). Incipient volume of the precursor was prepared by adding distilled water to known amounts of the precursor solution. This volume was then intimately mixed with the pretreated supports so as to make a paste. This paste was desiccated at room temperature for 16 h followed by drying at 373 K for 7 h and at 473 K for 14 h. The final step was calcination at 450°C for titania and 500°C for alumina. The active species loadings attempted were 1, 4, and 7% for the Titania support and 1, 5, 10, and 15 % for the alumina support based on the known amounts of precursor solutions used[47]. These loadings denote weight of Re_2O_7 as a weight percentage of catalyst. For all the samples, actual loading was different from that attempted because of reasons mentioned in the results section.

2.2 Characterization

2.2.1 Rhenium Analysis

The actual rhenium loadings for the supported rhenium oxide catalysts were determined by atomic absorption spectroscopy (AAS) using an Aanalyst 300 (Perkin-Elmer) spectrometer. More details are given elsewhere [37]

2.2.2 Raman Spectroscopy

The laser Raman spectra of the $\text{Re}_2\text{O}_7/\text{TiO}_2$ and $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalysts under ambient conditions were obtained by means of an Argon ion laser (Spectra Physics, Model 165). The 514.5 nm line was used as exciting source. Laser Power delivered at the sample was 15 to 40 mW. Scattered radiation from the sample was collected and directed to a Triplemate Spectrometer (Spex, Model 1877) coupled to an optical multichannel analyzer (Princeton Applied Research, Model 1463) with an intensified photodiode array detector thermoelectrically cooled to -35°C . About 200 mg of the supported rhena catalysts was pressed into self-supporting wafers and placed in a rotating sample cell, to avoid local heating effects.

2.2.3 UV-Visible Spectroscopy

UV-Vis spectroscopic studies were done using a Hitachi 20/120 spectrophotometer, which uses a Deuterium lamp for wavelengths from 190 to 340 nm and switches to a Tungsten lamp for obtaining wavelengths exceeding 340 nm. Barium sulfate, a high reflectivity material, is used as a standard. Catalysts pellets were supported on an absorbing background and placed in the sample holder. The spectra were obtained in absorbance mode.

2.2.4 Temperature Programmed Reduction

A mixture of 10% H_2/Ar at 1 bar pressure was used in a TPR apparatus (Altamira Instruments, Model AMI 100). The samples were precalcined *in situ* at 500°C in air for 15 minutes. The samples were then cooled to 50°C and dry argon was flushed to remove air. A mixture of hydrogen and argon at a molar ratio 1:9 was then passed at a flow rate of $17\mu\text{mol/sec}$. TPR measurements were carried out by increasing the temperature at a rate of 10°C/min up to 600°C . A TCD was used for monitoring hydrogen in the exit gas stream.

2.3 Reactor Setup

As shown in Fig. 3.1, a conventional differential reactor forms the heart of the experimental set-up for the reaction studies. This reactor houses about 200 mg catalyst mixed with quartz glass pieces. The catalyst and quartz glass particles were in the weight ratio of 1:5. Glass particles are added for dilution of the catalyst bed to avoid mass and heat transfer limitations. Size of both, catalyst and glass particles, was about 20 mesh. This catalyst-glass mixture is placed on the quartz wool at the center of this 300 mm long quartz reactor. Inner diameter of the reactor inlet is 10 mm, whereas that of the reactor outlet is 5 mm. These two sections are connected by a tapered section as shown in detail in Fig. 3.1. Inserted from the top in this reactor is a Chromel- Alumel thermocouple which has a temperature range of 0-800 °C. This thermocouple is the sensor in a feedback control loop, central to which is a PID controller (Fuji PXZ-4) capable of automatically tuning itself. Rotameters R1 and R2 (Eureka SRS/MG-5) are used for controlling the flow rates of propane and air, respectively. The flow rates are measured using a soap bubble meter (S1), which can give an accuracy of $\pm 1\%$.

Product gas analysis was performed using an online NUCON 5765 gas chromatograph at an oven temperature of 70 °C. A activated alumina column was used for separation of hydrocarbons and carbon oxides. Carbon oxides (CO and CO₂) were converted to methane by a methaniser in order to make them amenable to detection by FID.

2.3.1 Experimental Procedure

The catalysts were tested at a single flowrate of 40 ml/min and a constant 1:3 Oxygen/Propane volume ratio. The only variable, for a particular catalyst, was reaction temperature, which was varied from 300 to 450 °C. Room temperature analysis provided the reactor inlet conditions. Several runs were taken at each temperature to ensure steady state conditions.

2.4 Reactivity Calculations

Products of the reaction were propylene, carbon oxides, and small amounts of ethane and ethylene. The calculations of conversion, selectivity, yield, and turnover frequency were based on areas obtained from the chromatogram.

2.4.1 Conversion

For calculating conversions, the number of moles of reactants was assumed to be unchanged. This approach is justified since the conversion levels were low and the reactants were diluted in nitrogen. Areas were multiplied by corresponding sensitivity factors given by Dietz [48] (Table 3.1) to obtain true areas representative of the weight of each component. Values obtained were, thus, converted to represent moles of the components. The number of moles in was multiplied by mole fraction of each component in the exit to obtain moles of components in the exit gas. The conversion was calculated by the equation 2.1 given below.

$$\begin{aligned} \text{Conversion, \%} &= \frac{\text{Moles of propane converted}}{\text{Moles of propane in}} \times 100 \\ &= \frac{\text{Moles of propane in} - \text{Moles of propane out}}{\text{Moles of propane in}} \times 100 \end{aligned} \quad (2.1)$$

The carbon balance was also calculated and greater than 97% carbon atoms were accounted for.

2.4.2 Yield

The amount of propylene formed was represented by yield which was calculated as follows

$$\text{Propylene yield, \%} = \frac{\text{Moles of propylene formed}}{\text{Moles of propane in}} \times 100 \quad (2.2)$$

2.4.3 Selectivity

Selectivity for the reactions leading to formation of propylene was calculated as follows:

$$\text{Propylene selectivity, \%} = \frac{\text{Moles of propylene formed}}{\text{Moles of propane converted}} \times 100 \quad (2.3)$$

2.4.4 Turnover Frequency

For calculation of Turnover Frequencies (TOF), the actual Re₂O₇ present was assumed to be entirely on the surface of the support and all the active centers were assumed to be catalytically active. Turnover frequency was calculated as-

$$TOF, s^{-1} = \frac{\text{Moles of propylene formed / time}}{\text{Moles of Re present}} \quad (2.4)$$

2.4.5 Activation Energy

The activation energy (E) for reactions leading to propylene formation was calculated from the slope of a plot of ln(propylene yield) vs (1/T), where the temperature T is in K. This slope is E/R, where R is the ideal gas constant. This approximation is valid since differential conditions were assumed

Table 2.1. Dietz factor values [48]

Component	Dietz Factor
Propane	0.98
Propylene	1.02
Ethane	0.97
Ethylene	1.02
Methane	0.97

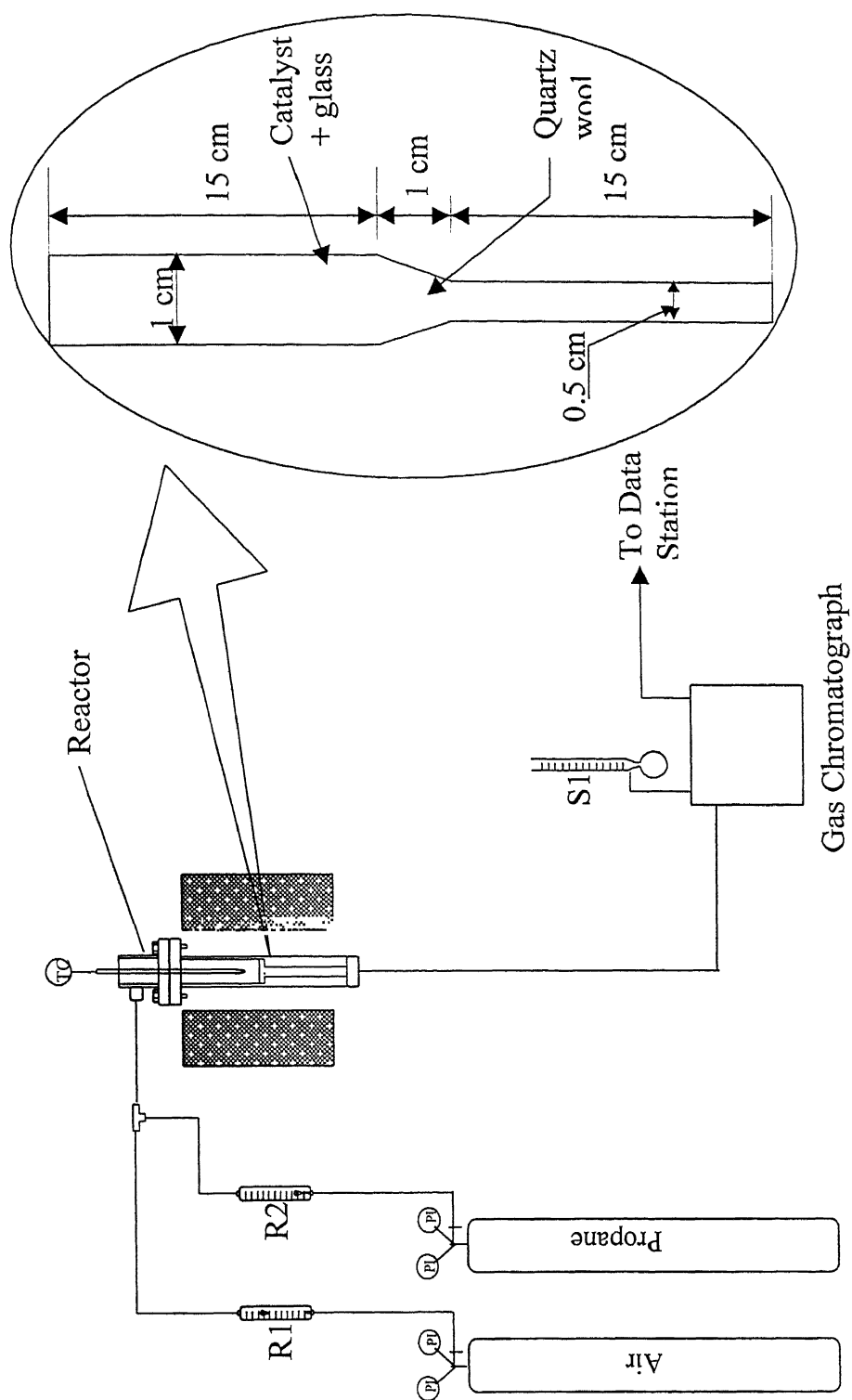


Fig 2.1: Experimental Setup for reaction studies

Several supported rhenium oxide catalysts were prepared and the rhenium content was determined. The attempted and actual rhenium content present in the catalyst along with the surface concentration (atoms/nm²) are presented in Table 4.1. The percentage of the rhenium oxide species retained and the fractional coverage based on a monolayer value of 8 atoms/nm² are also tabulated in table 3.1

Two catalysts, 2.5% Re₂O₇/TiO₂ and 7.8 % Re₂O₇/Al₂O₃, were chosen for the characterization studies, as these catalysts have close values of surface coverage.

3.1 Raman Spectroscopic Studies

In Fig. 3.1 the ambient Raman spectra of the catalysts mentioned above are presented in the 750-1050 cm⁻¹ region. The Re₂O₇/Al₂O₃ and Re₂O₇/TiO₂ catalysts show a sharp Raman band at ~980 cm⁻¹. However, for the Re₂O₇/TiO₂ catalyst, a shoulder is also observed at ~1000cm⁻¹. Both the spectra reveal weak bands at ~920 cm⁻¹. An additional weak band at ~790 cm⁻¹ is also observed for the Re₂O₇/TiO₂ catalyst, which is due to the TiO₂ support [26]. The Raman spectra of the alumina support is featureless.

3.2 UV-Visible Spectroscopic Studies

UV-vis spectra of the 7.8% Re₂O₃/Al₂O₃ and alumina support are presented in Fig. 3.3. In Fig. 3.4, spectra of the 2.5% Re₂O₇/TiO₂ catalyst and the titania support are shown. UV-vis spectra of the two catalysts and the supports were obtained in the diffuse reflectance mode under ambient conditions. In Fig. 3.5 and 3.6, the difference UV-visible spectra of the Re₂O₇/Al₂O₃ and the Re₂O₇/TiO₂ catalyst are shown. These spectra were obtained by subtracting the spectra of supports from those of supported rhenium oxide catalysts after proper normalization. The difference spectra should show the presence of the surface rhenium oxide species.

The two difference spectra, Fig. 3.5 and Fig. 3.6, reveal distinct differences in the wavelength range shown. The band at 235 nm is pronounced for the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst and somewhat diminished for the $\text{Re}_2\text{O}_7/\text{TiO}_2$ catalyst. Two distinct humps, at 340 and 425 nm, are present in the spectra of $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst. The $\text{Re}_2\text{O}_7/\text{TiO}_2$ catalyst clearly reveals bands at 207, 291, and 319 nm and shows a broad hump extending from 450 nm to 850 nm. This hump is absent in the spectra of pure titania.

3.3 TPR Studies

Temperature programmed reduction studies were also carried out over the supported rhenium oxide catalysts. Hydrogen concentration in the exit gas, which is directly related to the TCD signal, was obtained as a function of temperature and is shown in Fig. 3.2 for both the catalysts. Fig. 3.2 reveals that a single peak is present for each catalyst at different temperature. For the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst, the TPR maximum is at $\sim 340^\circ\text{C}$, whereas that for the $\text{Re}_2\text{O}_7/\text{TiO}_2$ catalyst is at $\sim 150^\circ\text{C}$.

3.4 Reactivity Studies

The oxidative dehydrogenation of propane reaction was carried out over the different supported rhenium oxide catalysts and the oxide supports. The main products formed during the reaction over the catalysts are propylene and carbon oxides. Trace amount of ethane and ethylene are also formed. No oxygenated compounds were detected. Blank runs were also carried out and no significant conversion was obtained.

3.4.1 Supports

Initially the ODH reaction was carried out over the pretreated titania and alumina supports used for making the supported rhenium oxide catalysts

3.4.1.1 Alumina support

The conversion and selectivity data obtained for the ODH of propane reaction are shown in Fig. 3.7. Fig. 3.7 reveals that the conversion of propane is small below 400°C . At higher temperatures, the conversion increases rapidly and a value of 1.1% is observed at 450°C .

This support was not found to be selective to propylene upto 380°C . However, propylene selectivity becomes significant at temperatures 400°C and higher and attains a value of 71.1 to 75.5%.

3.4.1.2 Titania support

The reaction data obtained over the titania support are shown in Fig. 3.8 in the temperature range of 300 to 450°C . From Fig. 3.8, it is observed that the conversion of propane continuously increases with temperature though the rate of increase was more at temperatures greater than 380°C . Conversion value at 330°C was 0.3% and at 450°C , it was 7.8%. An increase in selectivity for propylene was also observed with increasing temperature. However, the rate of increase in selectivity was more rapid in the initial temperature region and gradually flattens out at higher temperatures. The titania support shows a selectivity of 73.4 % at 450°C .

3.4.2 Supported Rhenia catalysts

The ODH of propane was carried out over four $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ and three $\text{Re}_2\text{O}_7/\text{TiO}_2$ catalysts and the data are presented in Fig. 3.9 to 3.12. Results below 380°C are not shown, since little conversion was observed at these temperatures

3.4.2.1 $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalysts

Fig. 3.9 shows the variation in propane conversion with loading at different temperatures for the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalysts. The curves are all nonintersecting. With an increase in loading, the conversions increased, reaching a maximum at an intermediate loading and then decreasing. At all temperatures, the highest conversions were obtained with the 7.8% $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst. These conversions were 0.6%, 1.1%, 3.4%, and 8.6% at 380, 400, 430, and 450°C , respectively. For a particular loading, conversion for all catalysts tested increased with increasing temperature. Though conversions continuously increased upto the 7.8% loading, the rate of increase was sharp only from 4.1% to 7.8% loading after which there was a significant decrease in conversion at 430 and 450°C . At 430°C , the conversion decreased from 3.4% to 2.4%, whereas at 450°C , conversion decreased

from 8.6% to 3.9% . At lower temperatures, decrease in conversion was not as pronounced.

The propylene selectivity for the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst and the alumina support are presented in Fig. 3.8 at different temperatures. Selectivity of the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst increased with loading from about 60-72% at 380°C to about 85-93% at 400°C. At 430 and 450°C, the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst showed a maximum in selectivity at the 7.8% loading and at higher loadings the selectivities decreased marginally. The maximum values of selectivities obtained for the 7.8% $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst were 93, 93.6, 93.6 and 92.1% at 380, 400, 430 and 450°C, respectively.

Very small amount of rhenia was observed deposited on the colder part of the reactor wall for the 7.8% $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst. For the 10.1% $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ sample, however, considerable amount of rhenium was observed deposited.

3.4.2.2 $\text{Re}_2\text{O}_7/\text{TiO}_2$ catalysts

Fig. 3.11 shows the variation in conversion with Re_2O_7 loading at different temperatures (380, 400, 430 and 450°C). At all temperatures, pure titania gave higher conversion than any of the supported rhenium oxide catalysts. The conversion increased with increasing temperature for all catalysts. The increase in conversion with temperature is due to activation energies involved. The lowest conversions, at all temperatures, were obtained with the 0.66% $\text{Re}_2\text{O}_7/\text{TiO}_2$ catalyst. These conversions were 0.2%, 0.4, 1%, and 1.7% at 380, 400, 430, and 450 °C, respectively. Among the $\text{Re}_2\text{O}_7/\text{TiO}_2$ catalysts tested, the highest conversions at all temperatures were obtained with the 2.5% loading catalyst. These conversions were 1.8%, 3.2%, 4.1%, and 5.5% at 380, 400, 430, and 450 °C, respectively. With higher loading, however, conversions declined. The 4.8% catalyst, at all temperatures, gave conversions higher than the 0.66% catalyst but lower than the 4% catalyst. This fall in conversion was almost as sharp as the rise in conversion from 0.66% to 4% loading. Conversions obtained with the 4.8% catalyst were 0.8%, 0.84%, 2.3%, and 3.5% at 380, 400, 430, and 450 °C , respectively. For this catalyst, 4.8% $\text{Re}_2\text{O}_7/\text{TiO}_2$, a considerable amount of rhenium was observed to be deposited on the colder part of reactor downstream, whereas small amount of rhenium was deposited for the 2.5% $\text{Re}_2\text{O}_7/\text{TiO}_2$ sample.

Two distinct propylene selectivity trends were observed for the $\text{Re}_2\text{O}_7/\text{TiO}_2$ catalysts as shown in Fig. 3.12. An increase and then a sharp decline in selectivity with loading was the trend prevailing at 380 and 400 °C. At higher temperatures, however, the selectivity continuously decreased. At 380 and 400°C, the maximum propylene selectivities were obtained with the 2.5% $\text{Re}_2\text{O}_7/\text{TiO}_2$ catalyst. This catalyst has a propylene selectivity of 77.3% at 400 °C. For the same temperature, however, at 4.8% loading, selectivity decreases to 53.7%. This is the lowest value of selectivity obtained with any $\text{Re}_2\text{O}_7/\text{TiO}_2$ catalyst tested. The 4.8% loading catalyst also shows the lowest selectivities at all temperatures except at 380 °C. At 380°C, the selectivity was 69.5% as compared to the 65.8% selectivity obtained with pure titania and the 0.66% loading catalysts. Selectivity- loading curves at 430 and 450 °C are similar.

The variation in selectivity with temperature did not show any distinguishable trend for loadings higher than 0.66%. For pure titania and the 0.66% catalyst, selectivity was found to increase with temperature.

3.4.3 Turnover frequency and activation energy

Turnover frequencies (TOF) and activation energies were calculated for all the catalysts tested by using the formula given in the preceding section. The results are summarized in table 3.2. Values of TOF at four temperatures are enumerated. As can be seen from Table 3.2, the turnover frequencies are a stronger function of temperature as compared to loading

Table 3.1 Actual and attempted Re₂O₇ loadings on Titania and Alumina supports

Support	Re ₂ O ₇ Loading Attempted %	Re ₂ O ₇ Loading Actual %	Surface Coverage, atom/nm ²	% Re ₂ O ₇ Retained	θ^a
Al ₂ O ₃	1	0.75	0.1	75	0.0125
	5	4.1	0.57	82	0.0712
	10	7.8	1.08	78	0.1350
	15	10.1	1.39	67	0.1740
TiO ₂	1	0.66	0.32	66	0.0400
	4	2.5	1.13	62	0.1410
	7	4.8	2.17	68	0.2710

$$^a \theta = \text{Fractional Coverage} = \frac{\text{Surface Coverage}}{\text{Monolayer Coverage}}$$

Theoretical Monolayer Coverage= 8 atom/nm² [54]

Table: 3.2: Turnover Frequencies and Activation Energies for Re₂O₇/TiO₂ and Re₂O₇/Al₂O₃ Catalysts.

Support	Re ₂ O ₇ Loading, %	TOF, s ⁻¹				Activation Energy, KJ
		380°C	400°C	430°C	450°C	
Al ₂ O ₃	0.75	0.0015	0.0035	0.0102	0.0188	164
	4.1	0.0005	0.0010	0.0027	0.0047	133
	7.8 ^a	0.0009	0.0017	0.0051	0.013	142
	10.1 ^c	0.0006	0.0012	0.0027	0.0041	115
TiO ₂	0.66	0.0024	0.0046	0.0129	0.0237	142
	2.5 ^b	0.0069	0.0120	0.0142	0.0188	53.2
	4.8 ^c	0.0014	0.0011	0.0038	0.0058	82.8

^aVery small amount of Rhenium found deposited on the colder part of reactor downstream^bSmall amount of Rhenium found deposited on the colder part of reactor downstream^cConsiderable amount of Rhenium found deposited on the colder part of reactor downstream

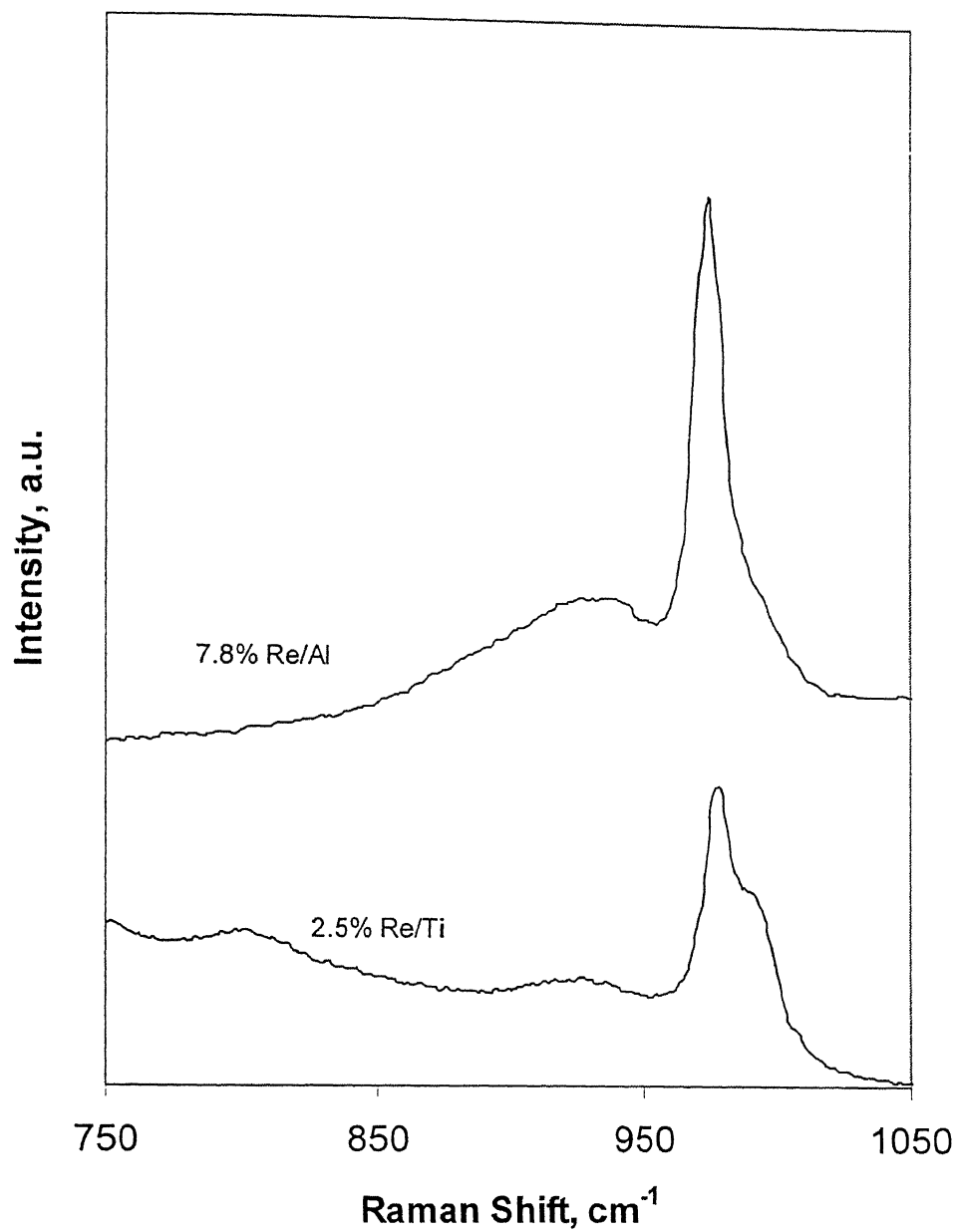


Fig 3.1: Ambient Raman spectra of the 7.8% $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ and the 2.5% $\text{Re}_2\text{O}_7/\text{TiO}_2$ catalysts

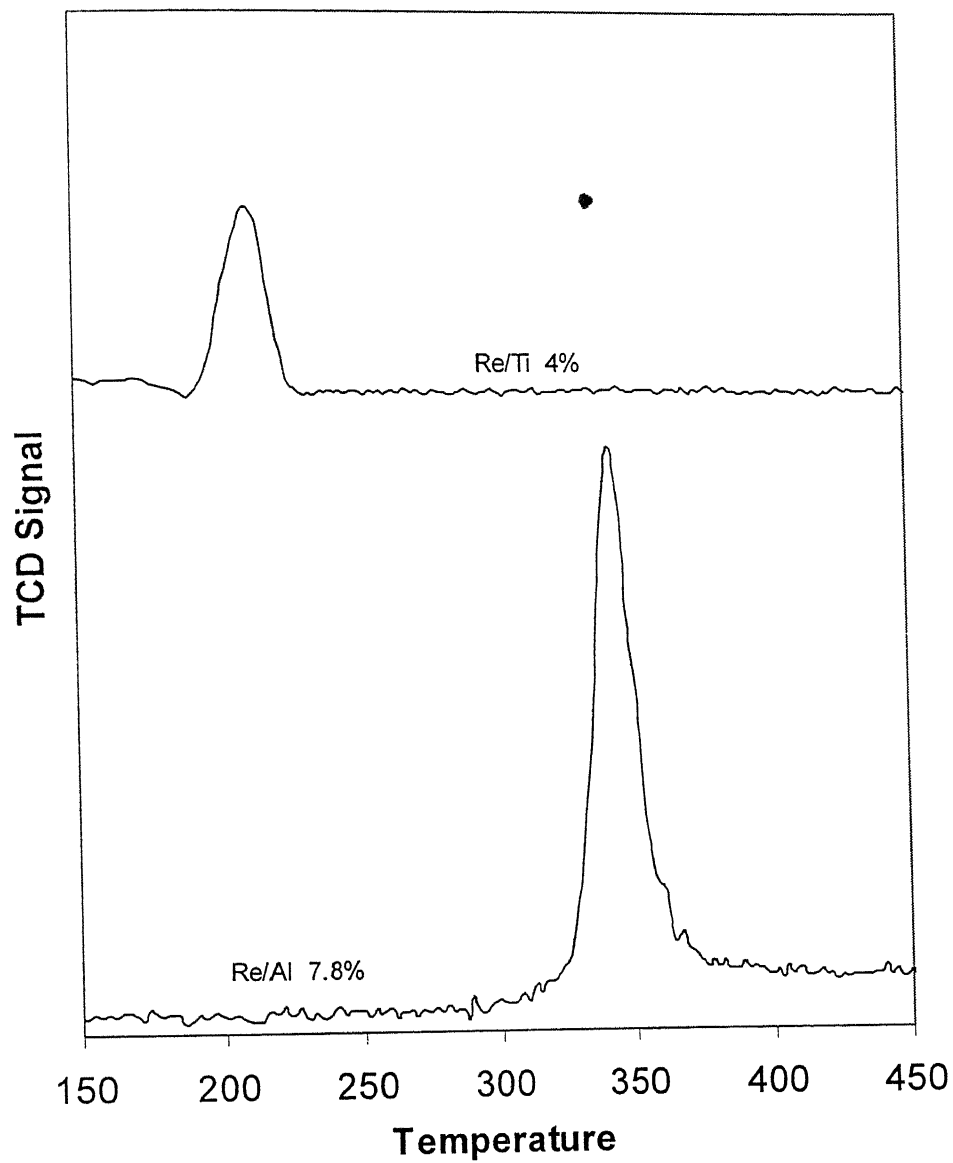


Fig 3.2: TPR plots of the 7.8% $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ and the 2.5% $\text{Re}_2\text{O}_7/\text{TiO}_2$ catalysts

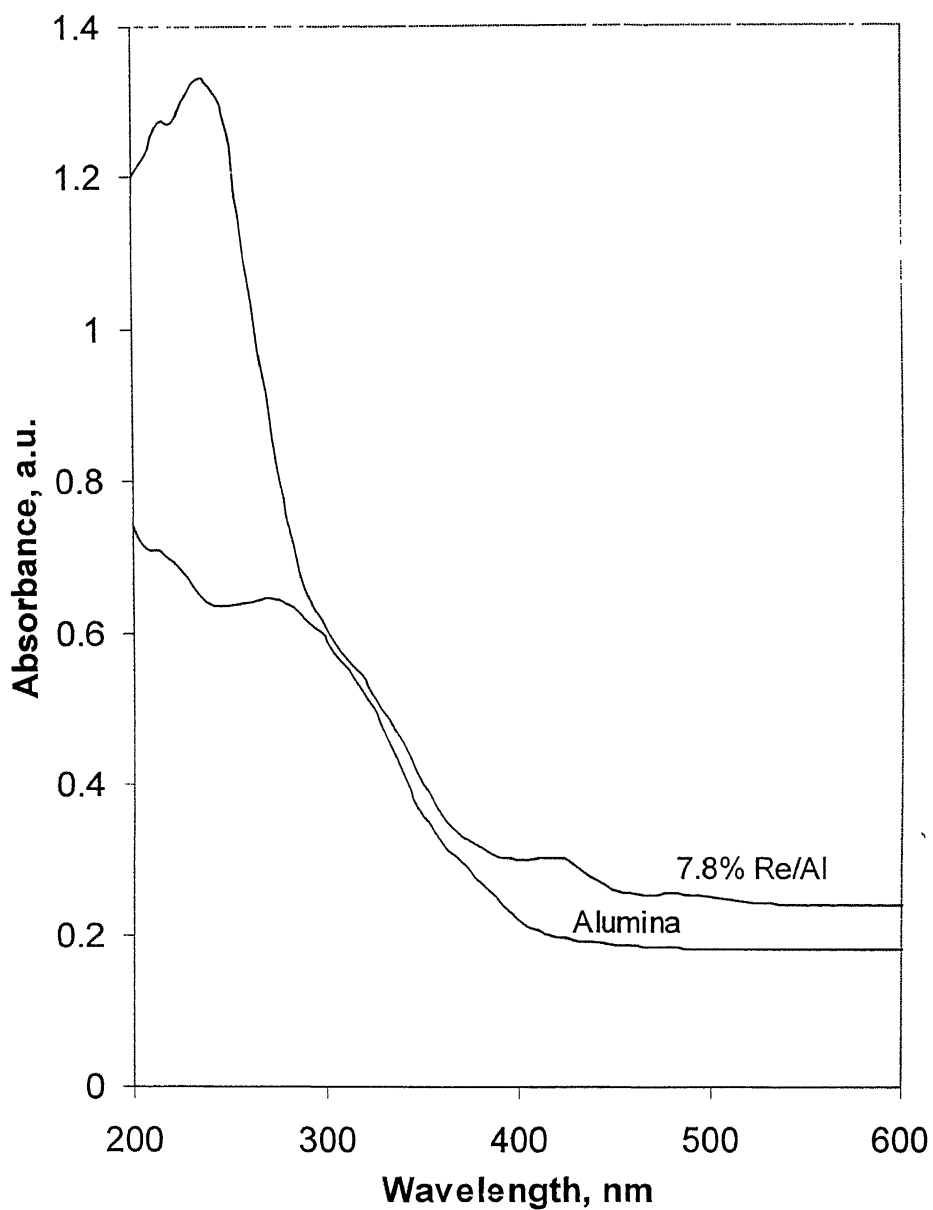


Fig 3.3: UV-Vis Spectra of the 7.8% $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ Catalyst and the alumina support under ambient conditions

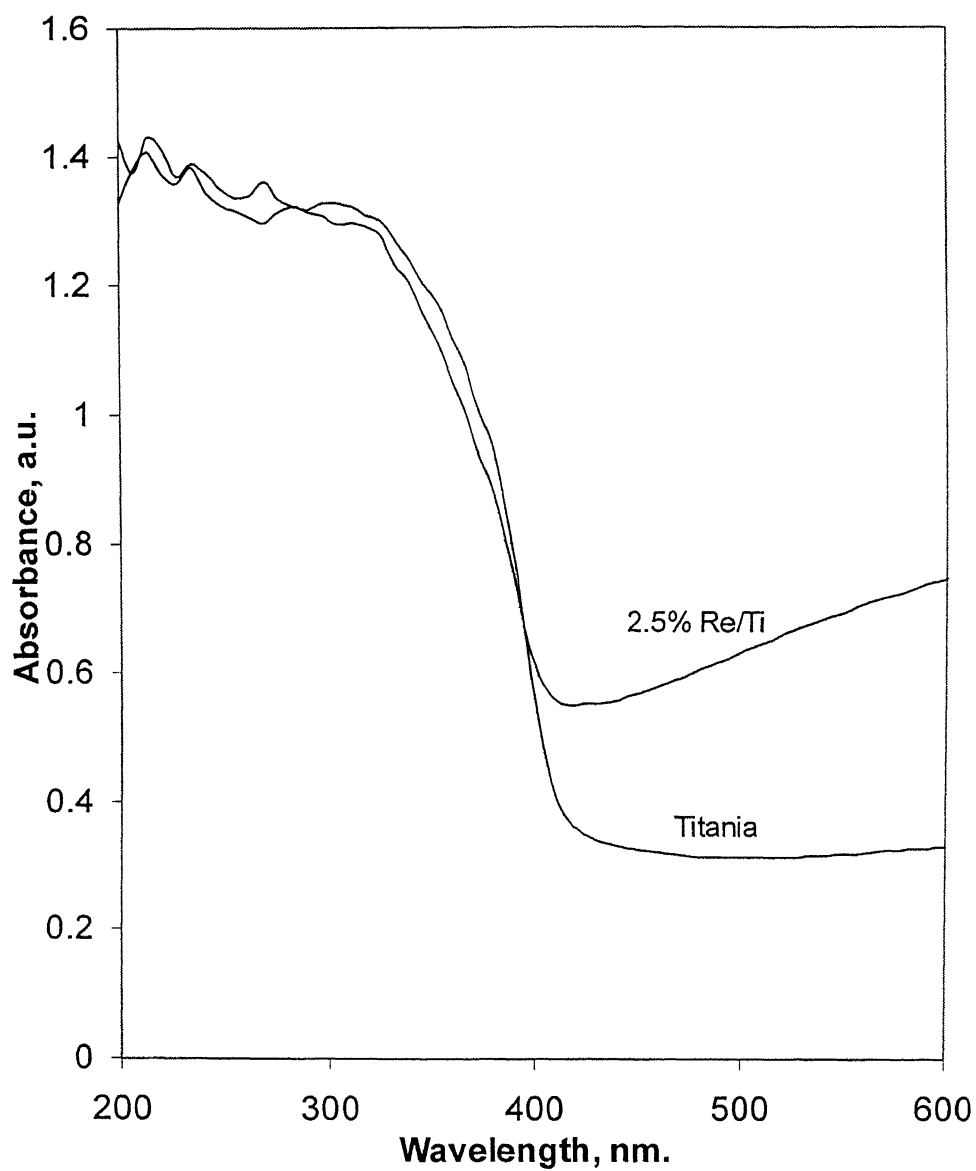


Fig 3.4: UV-Vis Spectra of the 2.5% $\text{Re}_2\text{O}_7/\text{TiO}_2$ Catalyst and the titania support under ambient conditions

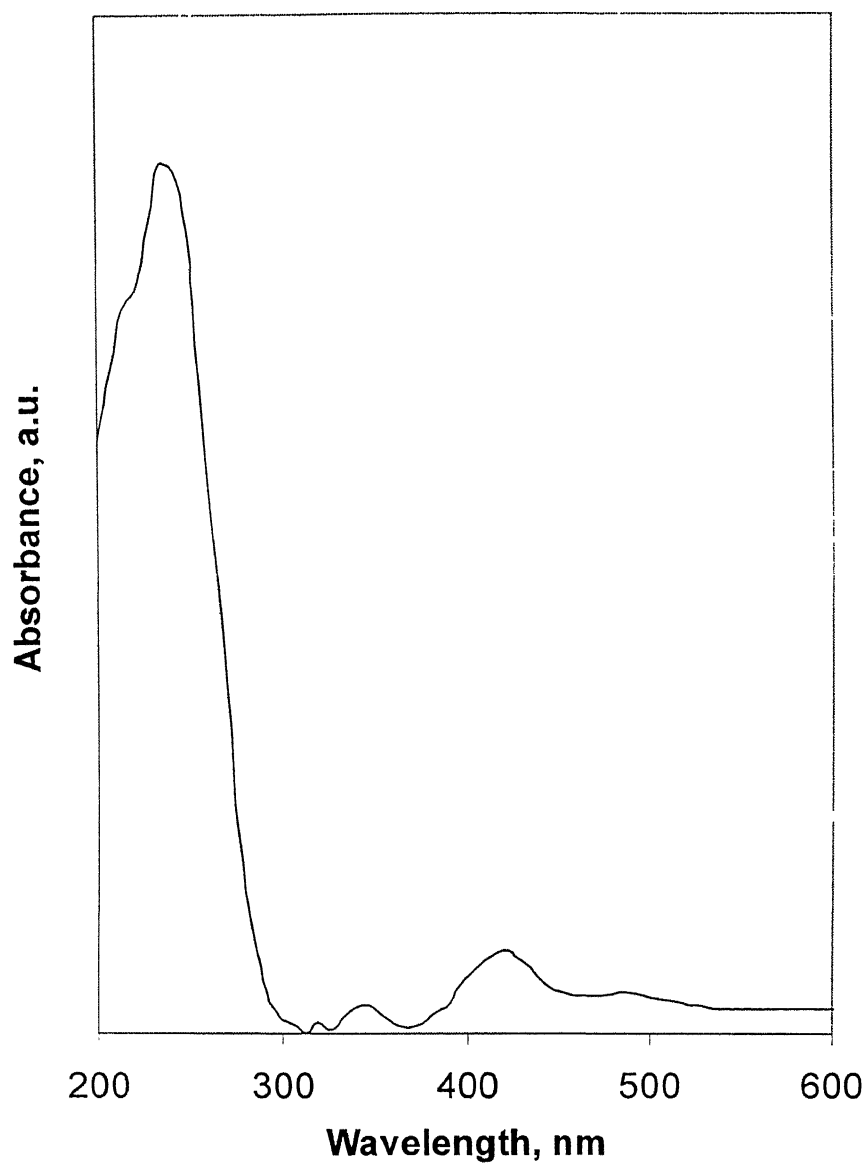


Fig 3.5: Difference UV-Vis Spectra of the 7.8% $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ Catalyst under ambient conditions

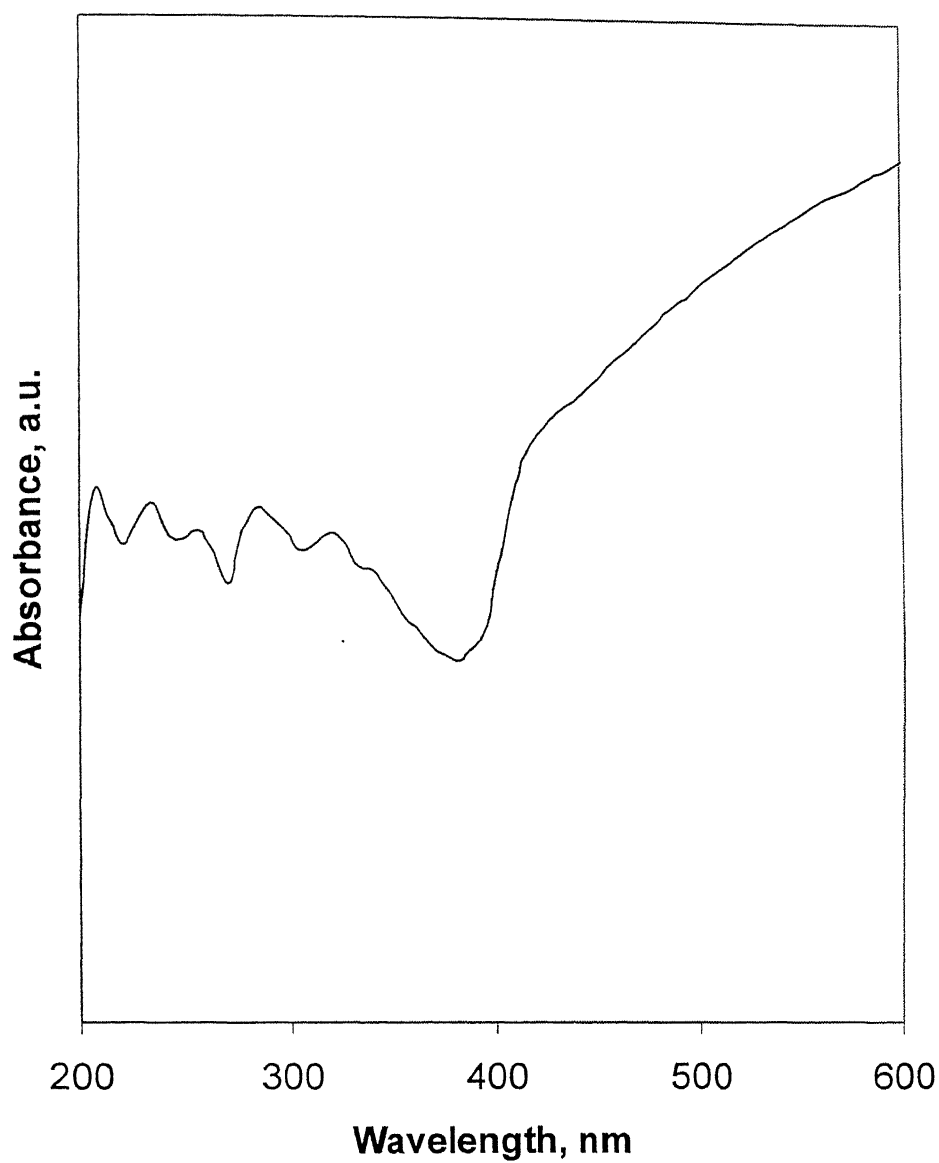


Fig 3.6: Difference UV-Vis Spectra of the 2.5% $\text{Re}_2\text{O}_7/\text{TiO}_2$ Catalyst under ambient conditions

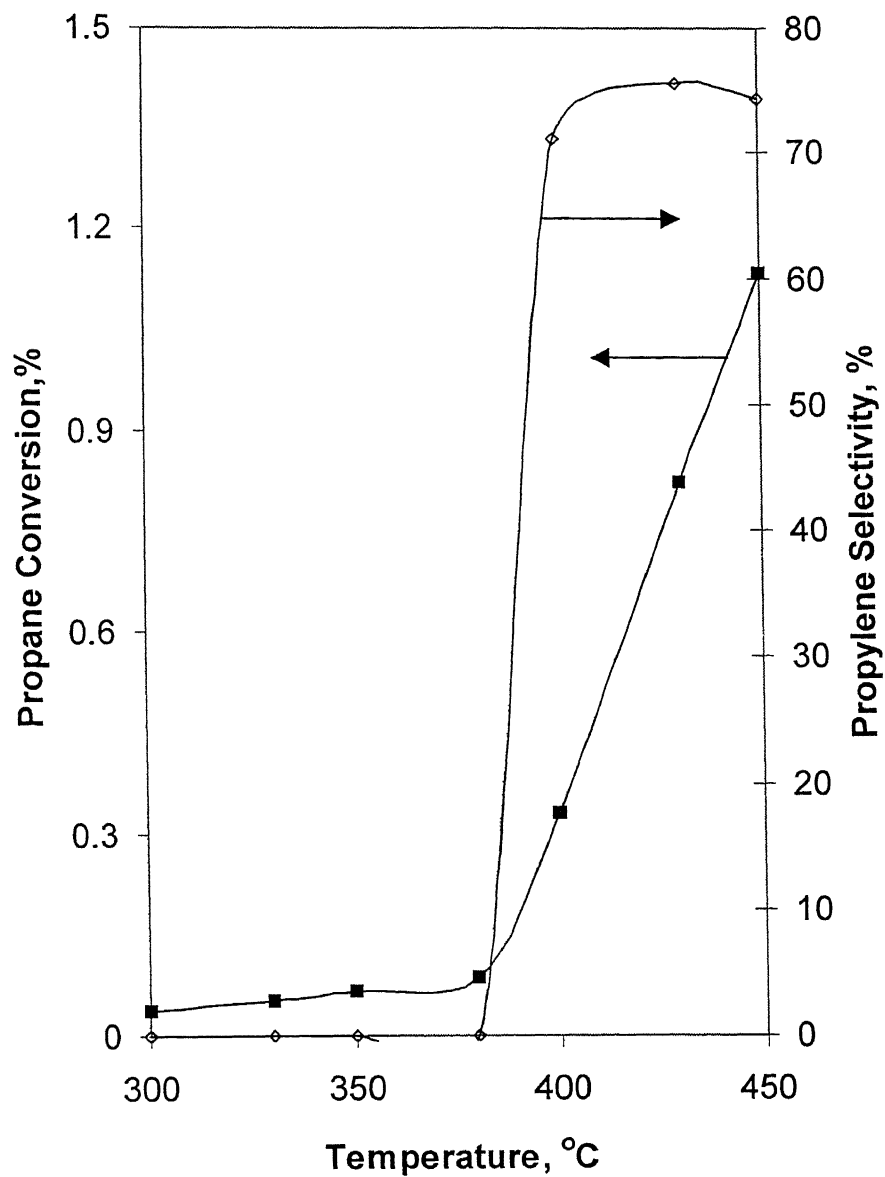


Fig 3.7: Variation of propane conversion and propylene selectivity with temperature for the alumina support

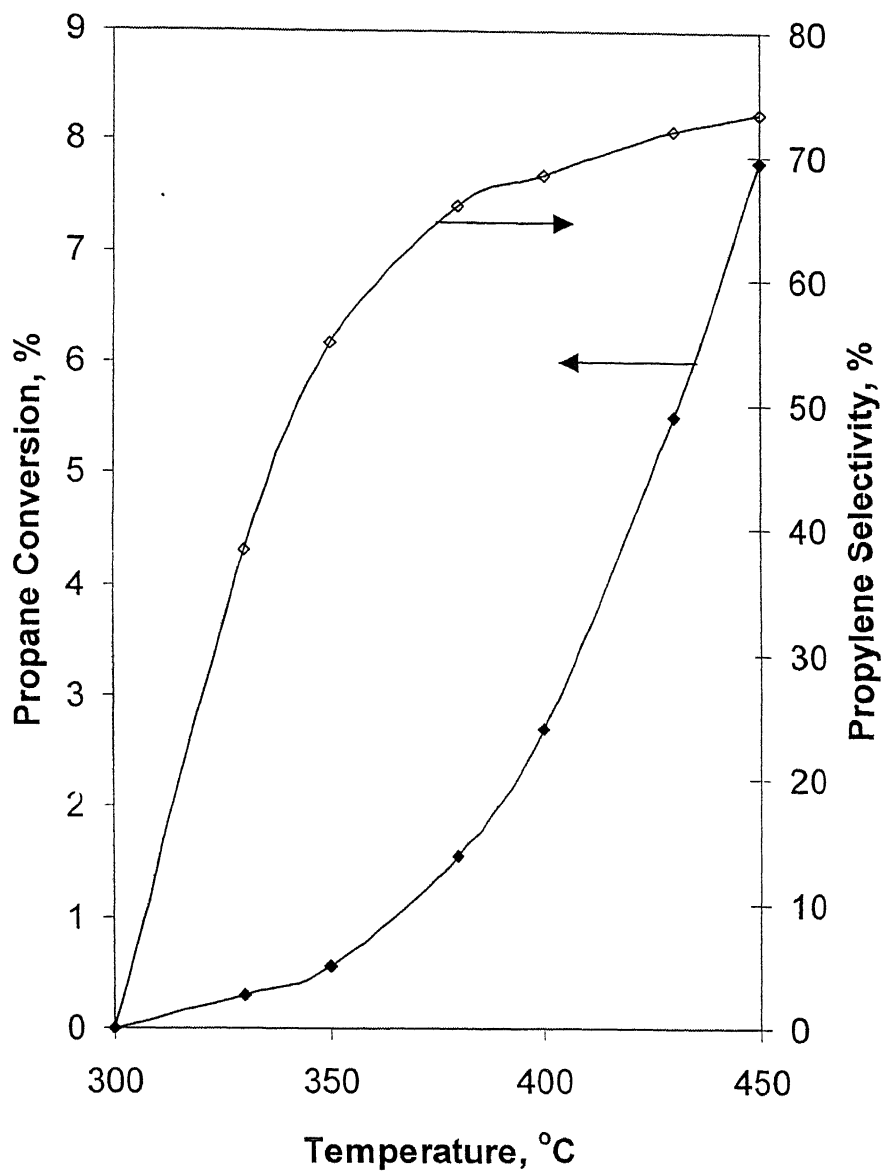


Fig 3.8: Variation of propane conversion and propylene selectivity with temperature for the titania support

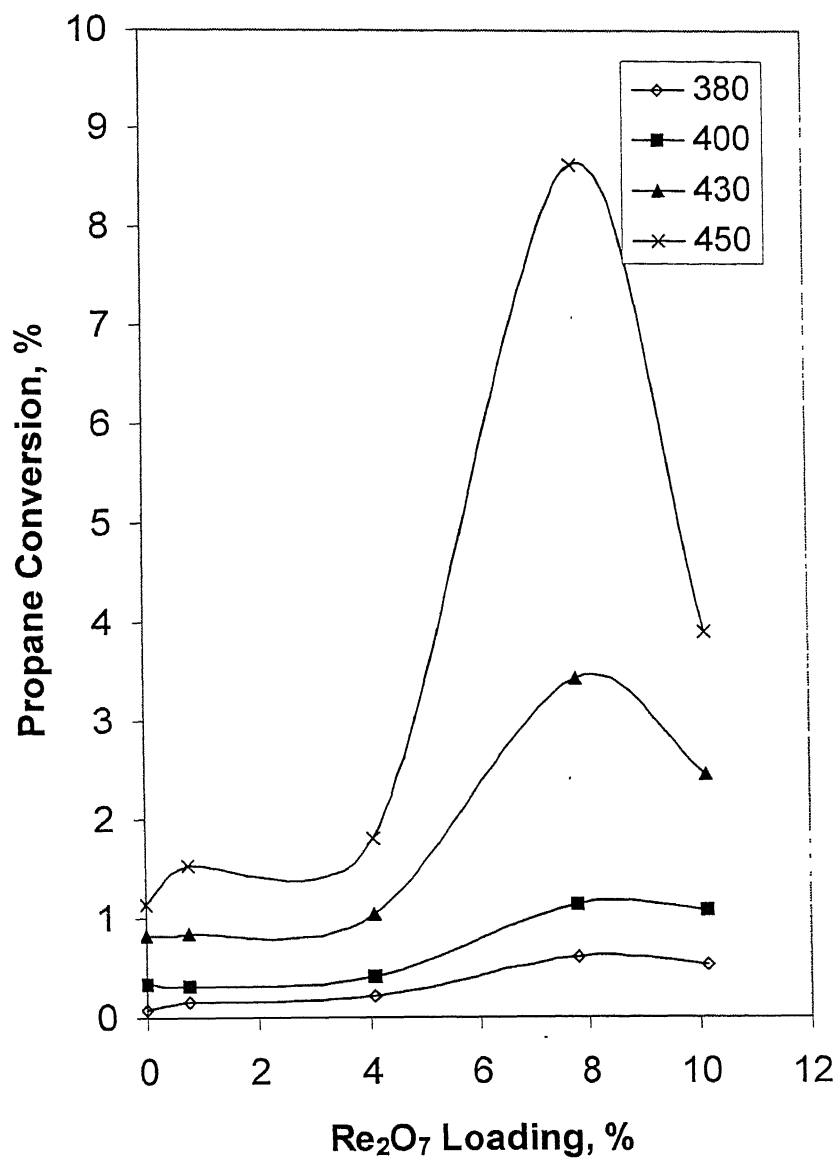


Fig 3.9: Variation of propane conversion with loading for $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalysts

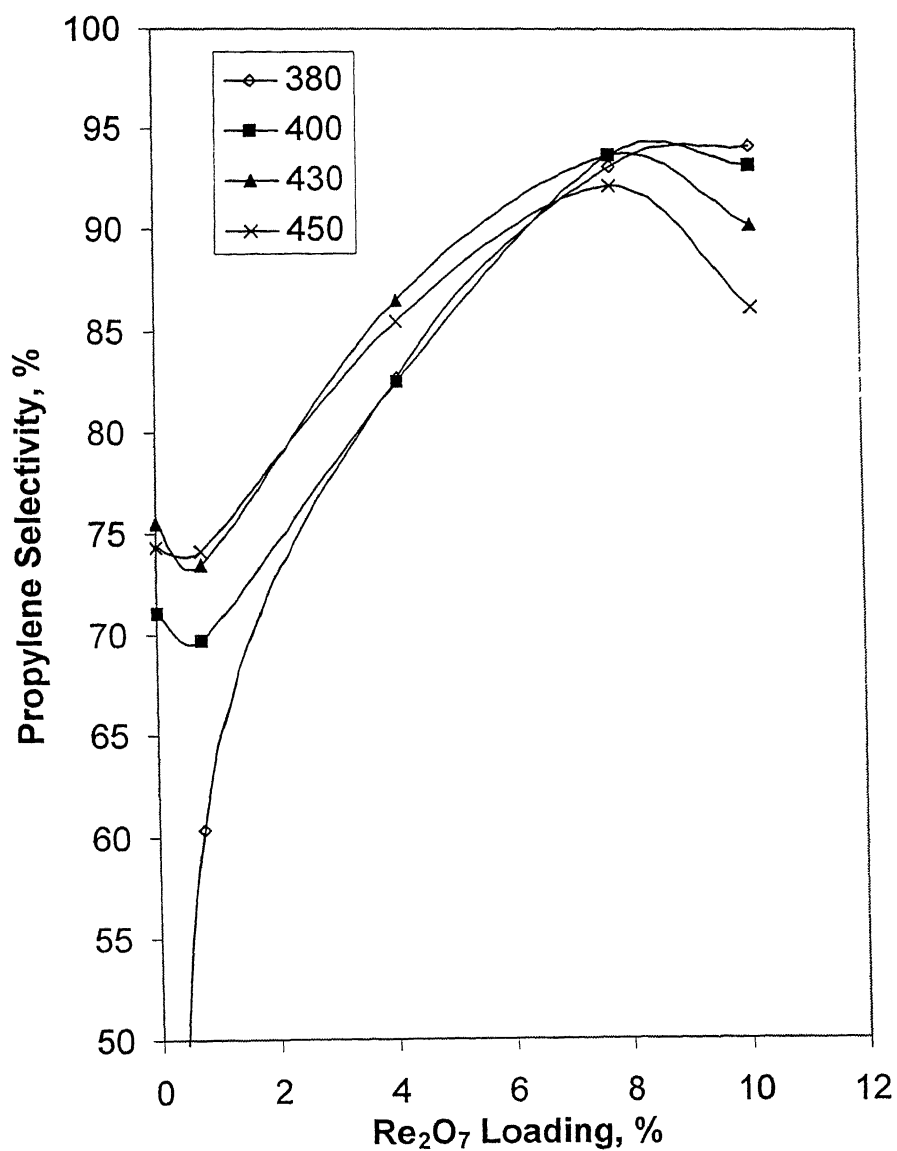


Fig 3.10: Variation of propylene selectivity with loading for $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalysts

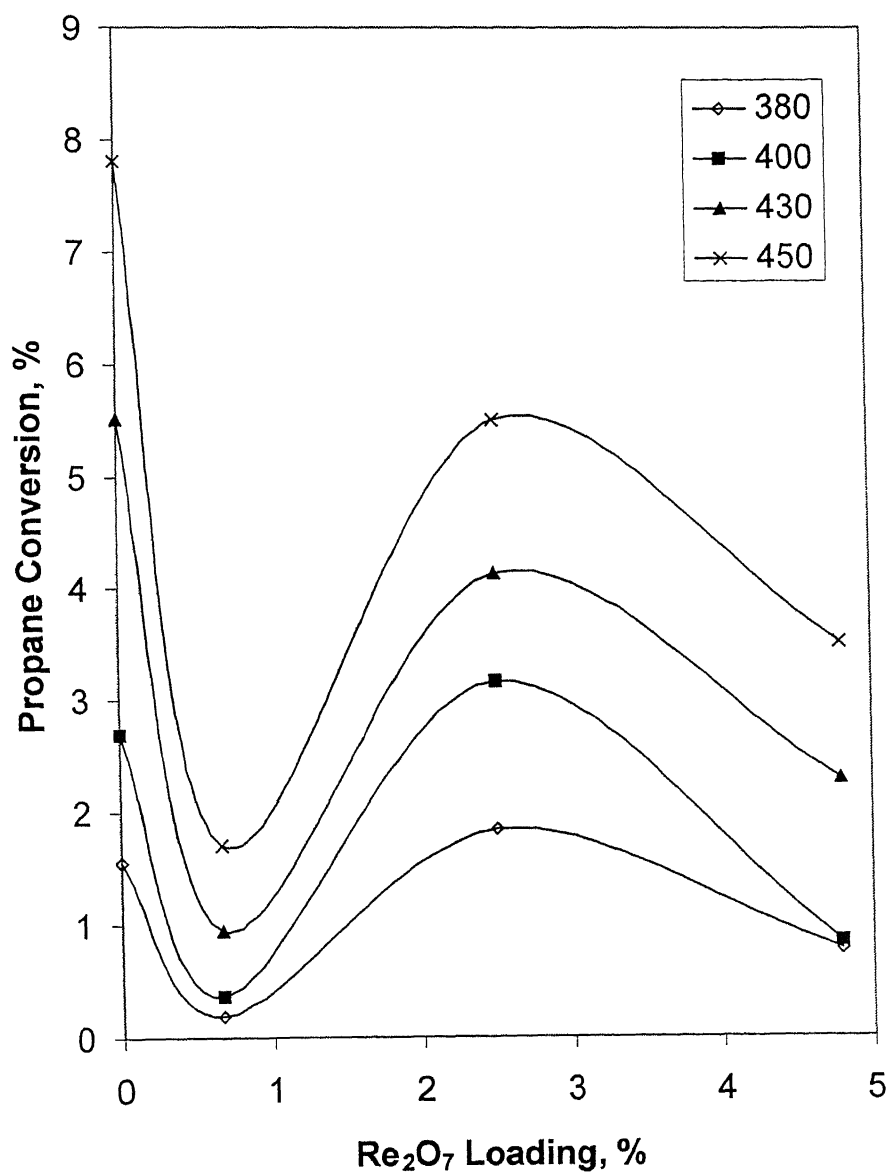


Fig 3.11: Variation of propane conversion with loading for $\text{Re}_2\text{O}_7/\text{TiO}_2$ catalysts

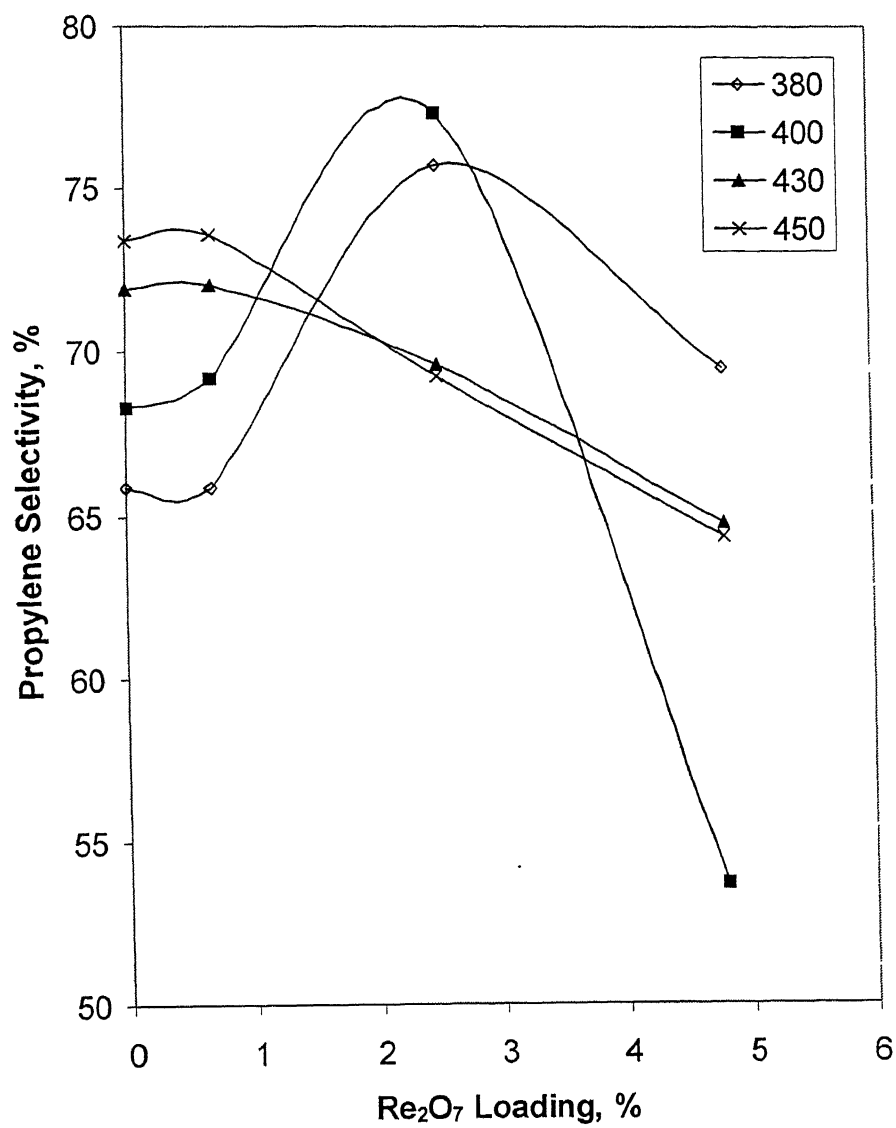


Fig 3.12. Variation of propylene selectivity with loading for $\text{Re}_2\text{O}_7/\text{TiO}_2$ catalysts

Supported rhenium oxide catalysts were prepared as mentioned in the experimental section. Actual loadings obtained were, however, different from those attempted. This is attributed to the volatile nature of surface rhenium oxide species at the temperatures encountered in the calcination step [34]. Hence the actual supported rhenium oxide loadings are invariably less than those attempted [34,37,49], as can be seen from Table 3.1. Since the percentage of active species retained on alumina support is more, it appears that alumina has a greater affinity for the rhenium oxide species. This may, however, be due to the larger surface area of the alumina support and additional studies are required to corroborate this observation.

4.1 Raman Spectroscopic Studies

Ambient Raman spectra of the 2.5% $\text{Re}_2\text{O}_7/\text{TiO}_2$ and the 7.8% $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalysts reveal Raman bands at ~ 980 and $\sim 920\text{ cm}^{-1}$ in the 750 to 1050 cm^{-1} region. Comparison of these Raman bands with those of known rhenium oxide structures reveals that there is a close similarity with ReO_4^- species in the solution. The Raman vibrations expected from a tetrahedral ReO_4^- species in solution are an asymmetric stretch of $\text{Re}=\text{O}$ at $\sim 920\text{ cm}^{-1}$, symmetric stretch of the same bond at $\sim 970\text{ cm}^{-1}$, and bending vibrations at $\sim 332\text{ cm}^{-1}$ [49]. Raman bands obtained at ~ 970 and 920 cm^{-1} confirm the presence of species similar to the ReO_4^- species in solution solutions. Under ambient conditions, all metal oxides are covered with hydroxyl groups [50]. According to a model proposed by Deo and Wachs, the hydrated surface metal oxide structures depend on the net pH at which the surface possesses zero surface charge [51]. This pH is determined by the combined pH of the surface and the metal oxide overlayer. In aqueous solutions, the only stable rhenium oxide species, at all values of pH and concentration, is ReO_4^- [52]. The surface Rhenia species is, therefore, present in its aqueous form and is isolated. These spectra are consistent with those obtained in previous Raman studies on this system

[5,13,19,24,26,33]. The rhenium oxide species present under ambient conditions is hydrated, regardless of loading [37,49].

Though the spectroscopy was performed in the range from 100 to 1300 cm^{-1} , the region of spectra below 600 cm^{-1} are sometimes dominated by absorbance by supports. However, no band corresponding to surface rhenium species is expected in this range other than the bending vibration at 300 cm^{-1} . The band was not observed in present studies since the analysis was limited to 750 cm^{-1} . Analysis of the spectra at lower wavenumbers indeed reveals a Raman band at 330 cm^{-1} . The shoulder observed at $\sim 1000 \text{ cm}^{-1}$ for the 2.5% $\text{Re}_2\text{O}_7/\text{TiO}_2$ catalyst can be attributed to dehydration induced by the laser used for obtaining the Raman spectra.

Under ambient conditions, the surface rhenium oxide species is hydrated and its structure is different from the structure of rhenium oxide species at high temperatures. At high temperatures commonly experienced during catalytic reactions, the surface moisture desorbs. Consequently, surface rhenium oxide species is anchored to the support. The ambient Raman spectra are, however, useful for the analysis of proper preparation of the catalyst and surface monolayer coverage.

Though Raman spectra of the catalysts tested were not obtained in dehydrated conditions, it is worthwhile to discuss the Raman spectra of $\text{Re}_2\text{O}_7/\text{TiO}_2$ and $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalysts under dehydrated conditions, since the catalytically active surface species is present only under dehydrated conditions. Fig. 4.1 shows the species on the support under ambient conditions when the surface is hydrated, and high temperatures when the surface is dehydrated. In the latter, the bond order of terminal metal-oxygen bond changes, thus, causing a shift in the position of its symmetric stretch from $\sim 970 \text{ cm}^{-1}$ to $\sim 1000 \text{ cm}^{-1}$. Many researchers believe in the presence of a dimeric species on the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst at higher loadings [15]. Their arguments have been strengthened by recent studies [35]. Despite these observations, it is clear that the surface rhenium oxide species under dehydrated conditions on the alumina and titania support are similar and independent of coverage [37].

4.2 UV-Visible Spectroscopic Studies

UV-visible spectroscopic studies on supported rhenium oxide catalysts are scarce. Table 4.2 lists absorption band positions of some transition metal oxyanion species [5]. The UV-vis spectra for pure supports agree with those obtained elsewhere [5,22,53].

For the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst, the 235nm band observed can be assigned to a species having tetrahedral symmetry (Ref. Table 4.2), which is the same as aqueous ReO_4^- ion. The band at 350nm indicates the possibility of presence of a species having C_{3v} symmetry. However, a species having this symmetry is not expected under ambient conditions and its origin is not known. A band has been observed by Wang and Hall [5] at 305nm for low loading $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalysts under dehydrated conditions.

For the $\text{Re}_2\text{O}_7/\text{TiO}_2$ catalyst, the band observed at 207nm again indicates the presence of a species with a tetrahedral symmetry. This conclusion can be strengthened by the presence of band at 235nm. It must be noted, however, that pure titania was found to have several absorption peaks in the 200-300nm region (Ref. Fig. 3.5), which complicate analysis in this region.

Though useful, the UV-Visible spectra were not found conclusive. Hence, it becomes imperative to use a powerful tool, like Raman spectroscopy, which can discriminate between various coexisting surface oxide species.

4.3 Temperature Programmed Reduction Studies

Temperature programmed reduction was used for studying the reduction behavior of the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ and the $\text{Re}_2\text{O}_7/\text{TiO}_2$ catalysts. TPR yields information over the temperature range where the reduction takes place, the amount of reducible oxygen, the oxidation state of the metal, the presence of various surface phases, possible interactions between the species, interaction with the support, and the factors that affect dispersion. During TPR, a programmed temperature increase coupled with a reducing atmosphere causes the reduction of the active species. A lower TPR reduction temperature is indicative of a facilely reducible active species, hence weak species-support interaction. A high TPR reduction temperature points to a species firmly adhered to the support. The very strong species-support interaction for $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst is well known [21], and has been attributed to high Lewis acidity of alumina support, leading to a stronger bridging

oxygen-support bond (Ref. Fig. 4.10). Supports are not expected to undergo reduction in the temperature range used for these studies and indeed no other reduction peak is observed in the present temperature range. For both the catalysts, a single reduction peak was observed, suggesting a single step reduction of $\text{Re}(+7)$ oxide to rhenium metal [20,21]. The TPR peak at 90°C , usually ascribed to the presence of water [49], was not observed for both the samples due to *in situ* pretreatment of the samples. A peak for methane, which results from reduction of volatile impurities which often get adsorbed on oxide surfaces, was also eliminated by the *in situ* pretreatment. A number of studies show a variation in TPR maximum with loading [20,21,54] for low rhenium oxide loadings. The variation found in these studies was pronounced only up to a loading of 0.5 atoms/nm^2 , after which the change was insignificant. This variation is usually attributed to chemical heterogeneity of the surface. However, these arguments appear weak in the light of recent studies [37], where TPR maximum values do not change with loading for coverages ranging from 0.1 to 2.17 atoms/nm^2 . These experiments [37] were performed with varying sample weight to elucidate that the shift owes its presence to mass transfer limitations instead of chemical heterogeneity of the support. Hence the TPR behavior of all the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalysts tested is expected to be identical. The same applies to the $\text{Re}_2\text{O}_7/\text{TiO}_2$ catalysts. However, this difference in temperature may be due to the different experimental set-ups used.

For the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst, the TPR peak is observed at 340°C , which is much higher as compared to the 240°C value observed for the $\text{Re}_2\text{O}_7/\text{TiO}_2$ catalyst. The higher value for the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst indicates stronger interaction between alumina support and the active species as compared to the titania support. The reducibility of titania supported species is more, hence the $\text{Re}_2\text{O}_7/\text{TiO}_2$ catalyst is expected to be more active than the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst. Since the interaction between support and the active species is through the bond between the bridging oxygen and the support, it can be inferred that the Re-O-Al bond is stronger than the Re-O-Ti bond (Ref. Fig. 4.1 [26]). It may also be pointed out that TPR maximum for $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ system is higher than any supported

Re_2O_7 catalyst, whereas that for $\text{Re}_2\text{O}_7/\text{TiO}_2$ catalyst is lower than any supported

Re_2O_7 catalyst [50]. In some studies [5], a species resisting reduction upto 450°C has been observed for the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst. No peak corresponding to this species was observed in present studies.

Thus, it appears that the surface rhenium oxide species is independent of surface coverage and oxide supports. However, the surface rhenium oxide species is more reducible on TiO_2 than on Al_2O_3 . The difference in reducibility is related to the Re-O-support bridging bond.

4.4 Chemical Reactivity Studies

Fig. 3.7 to Fig. 3.12 represent the results chemical of reactivity studies on pure alumina and titania supports and the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ and $\text{Re}_2\text{O}_7/\text{TiO}_2$ catalysts. For all the catalysts tested, conversion increased monotonically with temperature. Since little conversion was observed in empty reactor upto the highest temperature used for present studies, the contribution of homogeneous reaction is negligible. No peaks corresponding to oxygenates were observed in the chromatograms, thus indicating the absence of oxygen insertion occurring under the present conditions.

Comparison of the reactivity data in Figs. 3.7 and 3.8 reveal that pure alumina is less active than pure titania at all temperatures. Based on the propane conversion values, pure titania is 7.2 and 5.9 times more active than pure alumina at 400 and 450°C , respectively. The high activity exhibited by titania support is not unexpected, since titania is a good oxidation catalyst in the temperature range encountered in present studies [55]. Both the supports show an increase in propylene selectivity with temperature, which can be attributed to higher activation energy of the oxidative dehydrogenation (partial oxidation) reaction as compared to the total oxidation reaction, which yields carbon dioxide. The higher activation energy is due to much lower heat of formation of propylene as compared to that of CO_2 .

From above it is observed that alumina has a lower activity than the titania support. Comparisons of the conversions of the supports and the supported rhenium oxide catalysts in Figs. 3.9 to 3.12 reveals that the reactivity of the reactivity of the $\text{Re}_2\text{O}_7/\text{TiO}_2$ catalyst are comparable with the titania support, but the reactivities of the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalysts are more than the alumina support. Consequently, an increase in activity with

rhenium oxide loading on Al_2O_3 can be directly attributed to the surface rhenium oxide species. However, the effect of surface rhenium oxide species on titania on the activity for the ODH of propane is not conclusive, since the activity of the titania support is comparable or higher than the $\text{Re}_2\text{O}_7/\text{TiO}_2$ catalysts. The increase in activity of the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst with an increase in loading at all temperatures suggests that the surface rhenium oxide species forms the active phase. Furthermore, the increase in activity also corresponds to an increase in propane yield, which suggests that the surface rhenium oxide species is active for the oxidative dehydrogenation of propane to propylene. It has been observed previously that the surface rhenium oxide species is indeed active for the ODH of methanol to formaldehyde [26].

The similar activation energies observed for the propane to propylene reaction over the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalysts suggest that the rate-determining step is also similar. To determine the effect of each surface rhenium oxide active site, the propylene yields were normalized per rhenium oxide site in terms of the turnover frequency. The TOF of the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst were not constant, as seen from Table 3.2. and appeared to increase with loading except for the 10.1% $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst

The ODH of propane to propene can be considered a unimolecular reaction similar to the ODH of methanol to formaldehyde. For the ODH of methanol to formaldehyde over $\text{Re}_2\text{O}_7/\text{TiO}_2$ catalysts [33] and supported vanadium oxide catalysts [9], the turnover frequency was indeed observed independent of loading since the surface active sites in these catalysts were similar. The metathesis of propane, however, requires simultaneous participation of two propane molecules. Consequently, TOF for the metathesis reaction is observed to depend on loading for the $\text{Re}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst [54]. The TOF for ODH of propane was expected to be constant with loading, since the surface rhenium oxide sites on alumina have been observed to be similar [37] and the ODH of propane is a unimolecular reaction. However, since some of the rhenium volatilizes, a definite trend was not observed. In addition to this, the rhenium oxide loading used for calculating the TOF was over-estimated. Analysis of all the samples after the reaction for the rhenium oxide content would ideally be required.

Calculation of the true TOF for the $\text{Re}_2\text{O}_7/\text{TiO}_2$ catalyst was even more difficult, since two of the three catalysts had rhenium oxide volatilizing from the catalyst surface to

colder part of the reactor tube. Interestingly, the $\text{Re}_2\text{O}_7/\text{TiO}_2$ catalysts were more prone to rhenium volatilization than the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalysts, which was also observed in the preparation of these catalysts. As shown in Table 3.1, the titania supported retained lower amounts of rhenium oxide than the alumina support. Furthermore, due to comparable activities of the titania supported catalysts, the activity of the surface rhenium oxide species in the $\text{Re}_2\text{O}_7/\text{TiO}_2$ catalyst was difficult, if not impossible, to determine. Despite these factors, the TOF of the $\text{Re}_2\text{O}_7/\text{TiO}_2$ catalyst were calculated based on the actual Rhenium oxide initially present (Ref. Table 3.1). Comparison of the TOF of the $\text{Re}_2\text{O}_7/\text{TiO}_2$ catalysts with the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst suggests that the surface rhenium oxide species on TiO_2 is more active than the surface rhenium oxide species on Al_2O_3 . This observation appears to be justified, despite the comparable activity of the $\text{Re}_2\text{O}_7/\text{TiO}_2$ catalysts and pure titania since at higher coverages, contribution of the titania support is lower. For the ODH of methanol to formaldehyde, the activity of surface rhenium oxide species on titania was observed to be greater than the activity of surface rhenium oxide species on alumina [26] for low coverage (1%) samples. The difference in the activity of the same surface rhenium oxide species has been proposed to be due to the nature of the oxygen in the M-O-Support bridging bond [33].

The unexpected behavior of the $\text{Re}_2\text{O}_7/\text{TiO}_2$ catalysts is also observed in the propylene selectivity data. No distinct trend was observed for the $\text{Re}_2\text{O}_7/\text{TiO}_2$ catalysts as the rhenium oxide loading was increased. However, the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalysts reveal a significant increase in propylene selectivity with rhenium oxide loading except for the 10.1% $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst. As mentioned above, the 10.1% $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst showed significant volatilization of the surface rhenium oxide species. Consequently, the true rhenium oxide coverage present under reaction conditions is not known.

In summary, the surface rhenium oxide species prepared on TiO_2 and Al_2O_3 supports were structurally similar. However, the reducibility in hydrogen and reactivity with propane were significantly different. These differences were related to the strength/nature of the Re-O-Support bridging bond.

Table 4.1: UV-Vis absorption band positions of some solution transition metal oxyanion species [5].

Ion	Symmetry	$3t_2 \leftarrow t_1$	$2e \leftarrow t_2$	$5e \leftarrow a_2$	$5e \leftarrow 4e$
ReO ₄ ⁻	<i>Td</i>	205	235	-	-
MoO ₄ ²⁻	<i>Td</i>	205	230	-	-
WO ₄ ²⁻	<i>Td</i>	-	200	-	-
CrO ₄ ²⁻	<i>Td</i>	273	373	-	-
HReO ₄	<i>C3_v</i>	210	-	230	295
HMoO ₄ ⁻	<i>C3_v</i>	120	-	230	260
HCrO ₄ ⁻	<i>C3_v</i>	260	-	350	450

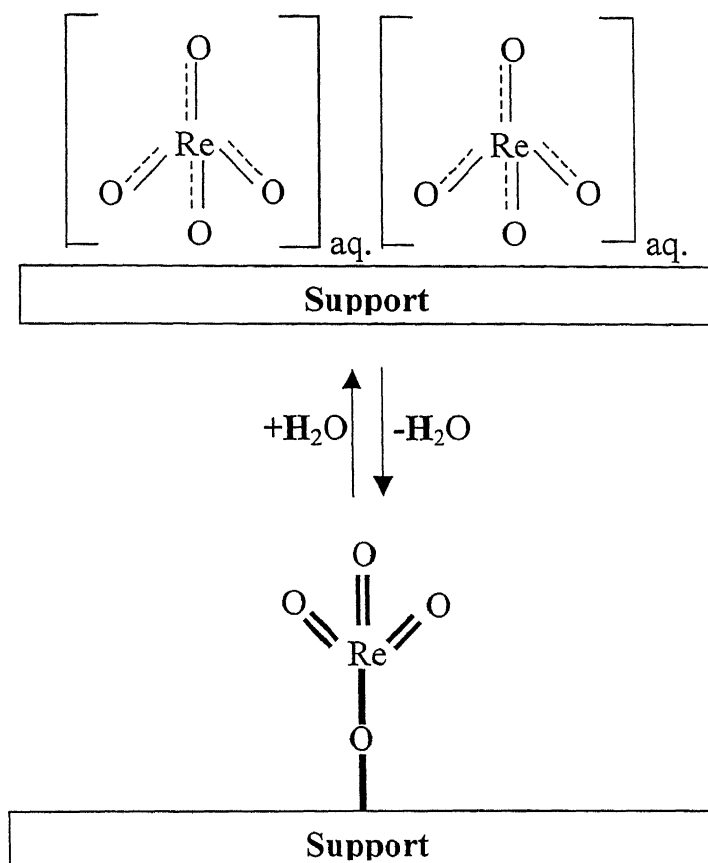


Fig 4.1: Two dimensional model of the supported Re_2O_7 catalysts under dehydrated and under hydrated conditions.

Conclusions and Recommendations

Rhenium oxide remarkably alters catalytic properties of titania and alumina supports, which can be seen from results of the studies. Based on the physical characterization and chemical reactivity studies, the following conclusions can be made.

From the results of Raman spectroscopy and, to some extent, those obtained with UV-Vis spectroscopy, presence of a surface rhenium oxide species having similar structure on both titania and alumina supports is proposed. The catalytic properties of this surface rhenium oxide species depend significantly on the support. This is attributed to the difference in the environment of the two surface species. From the amount of rhenium oxide retained on the support after calcination and the TPR experiments, it is concluded that alumina support has a greater affinity for surface rhenium oxide species as compared to the titania support. The strength/nature of bridging oxygen-support bond for the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalysts is different from that for the $\text{Re}_2\text{O}_7/\text{TiO}_2$ catalysts despite the presence of similar surface rhenium oxide structures. It is also inferred that greater reducibility of the surface rhenium oxide species leads to higher activity and lower selectivity for the oxidative dehydrogenation of propane

Recommendations for future work

The results displayed by $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalysts instigate our interest further into the factors that go into making them more active and selective than the $\text{Re}_2\text{O}_7/\text{TiO}_2$ catalysts.

It is recommended that catalysts of closer values of Re_2O_7 loadings on alumina be studied to locate the optimum loading of Re_2O_7 , which can give high activity and selectivity. It is also recommended to make further investigations into the role played by supports, especially as the Re_2O_7 loading is increased. The possibility of decrease in activity due to rhenium being washed off the support at higher loadings cannot be overruled. Attempts can be made to stabilize Re_2O_7 on supports so that the effect of loading can be better studied. This stabilization can be attempted through the use of additives to the Re_2O_7 catalysts. Determination of final rhenium content of the catalysts

showing a wash off, combined with study of coke deposition on the catalysts is also recommended. The high activity displayed by $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst for the metathesis reaction is often attributed to the acidic nature of support, and indeed the activity is increased by one to two orders of magnitude by the use of $\text{Al}_2\text{O}_3\text{-SiO}_2$ support [30], hence mixed oxide supports can be tested for the ODH reaction. High calcination temperatures have been shown to have a positive effect on the activity of $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst [8]. The effect of increased calcination temperature, thus, can also be studied. Activity of the metathesis catalyst increases on addition of V_2O_5 , MoO_3 , or WO_3 [31], hence the effect of addition of these oxides to $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalysts for the ODH of propane can also be studied.

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